

University of Windsor

Scholarship at UWindor

Electronic Theses and Dissertations

Theses, Dissertations, and Major Papers

1982

PREPARATIVE AND SPECTROSCOPIC STUDIES OF SOME LOW OXIDATION STATE DERIVATIVES OF INDIUM.

LUIS IVAN. VICTORIANO

University of Windsor

Follow this and additional works at: <https://scholar.uwindsor.ca/etd>

Recommended Citation

VICTORIANO, LUIS IVAN., "PREPARATIVE AND SPECTROSCOPIC STUDIES OF SOME LOW OXIDATION STATE DERIVATIVES OF INDIUM." (1982). *Electronic Theses and Dissertations*. 3177.

<https://scholar.uwindsor.ca/etd/3177>

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.

CANADIAN THESES ON MICROFICHE

I.S.B.N.

THESES CANADIENNES SUR MICROFICHE



National Library of Canada
Collections Development Branch

Canadian Theses on
Microfiche Service

Ottawa, Canada
K1A 0N4

Bibliothèque nationale du Canada
Direction du développement des collections

Service des thèses canadiennes
sur microfiche

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE

PREPARATIVE AND SPECTROSCOPIC STUDIES OF SOME
LOW OXIDATION STATE DERIVATIVES OF INDIUM

by



LUIS IVAN VICTORIANO

A Dissertation
submitted to the Faculty of Graduate Studies
through the Department of
Chemistry in Partial Fulfillment
of the requirements for the Degree
of Doctor of Philosophy at
The University of Windsor
Windsor, Ontario, Canada
1981

© Luis Ivan VICTORIANO 1981

All Rights Reserved

766084

A mi madre Florina,
y a la memoria de mi padre, Luis

ACKNOWLEDGEMENTS

The author is indebted to the following persons, who contributed in varying degrees to the outcome of this Dissertation:

Dr. Joseph D. Artiss	Dr. John M. McIntosh
Mr. Robert Campbell	Dr. Akhtar Osman
Dr. Allan F. Clark	Dr. Cynthia M. Owens
Dr. John E. Drake	Mr. Clovis Peppe
Mr. Mike Fuerth	Dr. John S. Poland
Mr. Ian Grove	Dr. Farouq F. Said
Dr. Jacob J. Habeeb	Dr. Richard S. Steevensz
Dr. Raymond T. Hemmings	Dr. Michael J. Taylor
Dr. J. Lawrence Hencher	Dr. Dennis G. Tuck
Dr. Layla N. Khasrou	Dr. Andrew Turek
Dr. Bruce R. McGarvey	Mr. Samuel Zhandire

Apologies are offered for any omission of deserving names.

ABSTRACT

The oxidation of indium(II) complexes $\text{In}_2\text{X}_6^{2-}$ with halogen Y_2 yields the anionic halogeno mixed complexes InX_3Y^- . Similar oxidations of the indium(I) anions InX_2^- furnish InX_2Y_2^- complexes, all as salts with tetraalkylammonium cations. The far - infrared and Raman spectra establish that the anions are indeed the mononuclear mixed - ligand species. Similar reactions, in which the metal - metal bond in $\text{In}_2\text{X}_6^{2-}$ is cleaved with methyl halides MeX , afford MeInX_3^- ($\text{X} \neq \text{Y} = \text{Cl}, \text{Br}, \text{I}$). The mechanism of rupture of the metal - metal bond is discussed.

^{115}In -NMR studies are reported for InX_4^- , $\text{In}_2\text{X}_6^{2-}$, InX_3Y^- , InX_2Y_2^- and InX_4^- in the presence of X^- (X and Y as before) in various nonaqueous solvents. The results confirm and extend previous studies of the nonaqueous solution chemistry of these complexes.

The macrocycles dibenzo-18-crown-6-ether and 1,4,8,11-tetraazacyclotetradecane form adducts with InX_2 and InX_3 , but not with InX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Vibrational spectroscopy shows that the products $\text{In}_2\text{X}_4\text{L}$ (L = macrocycle) should be formulated as $[\text{InL}][\text{InX}_4]$. With InX_3 and dibenzo-18-crown-6-ether the spectra reveal the presence of InX_4^- anions and linear InX_2^+ species. The reaction of cyclam and InX_3 yields products

formulated as $[\text{In}(\text{cyclam})_2][\text{InX}_4]_3$.

The neutral indium(II) compounds $\text{In}_2\text{X}_4(\text{Et}_3\text{P})_2$, $\text{In}_2\text{X}_4(\text{TMED})_2$ and $\text{In}_2\text{X}_4(\text{TMED})_2\text{C}_6\text{H}_6$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{TMED} = \text{N}, \text{N}, \text{N}', \text{N}'$ -tetramethylethylenediamine) have been prepared by the reaction of InX_2 and donor in benzene or toluene. With several other neutral donors, and in all systems involving InCl_2 , decomposition to indium metal is the predominant process. Analysis of the vibrational spectra demonstrates that these structures involve $\text{X}_2\text{In} - \text{InX}_2$ kernels. Slight revisions are proposed to previous discussions of the infrared spectra of $\text{In}_2\text{X}_6^{2-}$ anions.

Several synthetic routes to prepare organoindium(II) derivatives are described. Such reactions invariably lead to production of indium metal. Possible mechanisms for this decomposition are discussed. A convenient method for the preparation of cyclopentadienylindium(I) is reported.

TABLE OF CONTENTS

Abstract	vi
Acknowledgements	v
List of Tables	xi
List of Figures	xiii
Table of Abbreviations	xiv
GENERAL CONSIDERATIONS	
A. Introduction	1
B. Structure and bonding in Indium Derivatives	2
C. The present work	3
D. Experimental methods	4
CHAPTER 1 - THE PREPARATION AND VIBRATIONAL SPECTRA OF THE InX_3Y^- , InX_2Y_2^- AND MeInX_3^- SPECIES ($\text{X} \neq \text{Y} = \text{Cl}, \text{Br}, \text{I}$)	
1.1 Introduction	9
1.2 Experimental	10
1.3 The cleavage of the $\text{In(II)} - \text{In(II)}$ bond	15
1.4 The vibrational spectra of the InX_3Y^- anions	18
1.5 The vibrational spectra of the InX_2Y_2^- anions	23
1.6 The MeInX_3^- anions	25
1.7 Conclusions	28
CHAPTER 2 - ^{115}In -NMR STUDIES OF ANIONIC INDIUM SPECIES IN NONAQUEOUS SOLUTION	
2.1 Introduction	29
2.2 ^{115}In -NMR spectroscopy, general	30
2.3 Solvent and concentration effects	31
2.4 Tetrahalogenoindate(III) anions	36
2.5 Hexahalogenodiindate(II) anions	38
2.6 The $\text{InX}_4^-/\text{X}^-$ systems	40

2.7	Mixed halogeno species InX_3Y^- , InX_2Y_2^- and InX_2YZ^-	48
2.8	Miscellaneous organoindium compounds	57
2.9	Conclusions.	
CHAPTER 3. - COMPLEXES OF In(I) AND In(III) WITH SOME MACROCYCLIC LIGANDS.		
3.1	Introduction	59
3.2	Experimental	61
3.3	Ligand complexation	63
3.4	Indium monohalides	65
3.5	Indium dihalides	65
3.6	Indium trihalides	69
3.7	Organoindium halides	74
3.8	Conclusions	75
CHAPTER 4. - SOME NEUTRAL ADDUCTS OF In_2Br_4 and In_2I_4		
4.1	Introduction	78
4.2	Experimental	80
4.3	General	83
4.4	Vibrational spectroscopy	84
4.5	Triethylphosphine complexes	87
4.6	N,N,N',N' -tetramethylethylenediamine complexes	91
4.7	Reaction pathway	94
4.8	Conclusions	95
CHAPTER 5. - SYNTHETIC APPROACHES TO SOME LOW VALENT ORGANO-INDIUM COMPLEXES		
5.1	Introduction	96
5.2	Experimental	98

5.3	General	103
5.4	Reduction of organoindium(III) species	105
5.5	Alkylation and arylation of indium(II) compounds	107
5.6	Comproportionation of organoindium(III) species and indium(I) iodide	108
5.7	Reactions of indium(I) halides and organo- lithium compounds	109
APPENDIX A. - THE SYSTEM $\text{InCl}_4^-/\text{Cl}^-$		110
REFERENCES		112
VITA AUCTORIS		120

LIST OF TABLES

Table 1. Melting points and analytical results for $[(C_4H_9)_4N]InX_2Y_2$ salts	12
Table 2. Analytical results for the $[(C_4H_9)_4N] MeInX_3$ salts	14
Table 3. The vibrational spectra of InX_3Y^- anions	19
Table 4. The vibrational spectra of $InX_2Y_2^-$ anions	24
Table 5. The vibrational spectra of $MeInX_3^-$ anions	27
Table 6. Concentration and solvent dependence of the ^{115}In resonance of $[(C_6H_5)_4P] [InCl_4]$ at 27°C	32
Table 7. ^{115}In resonances for InX_4^- and related compounds in non-aqueous solution	37
Table 8. Experimental ^{115}In resonances (in ppm) for InX_nY_{4-n} anions ($X \neq Y = Cl, Br, I$) in CH_2Cl_2 solution	51
Table 9. Mean ^{115}In resonances for $InX_nY_{4-n}^-$ anions in dichloromethane	47
Table 10. Analytical results for indium complexes with macrocyclic ligands	62
Table 11. The vibrational spectrum of In_2X_4L and $InAlCl_4(crown)$ below 500 cm^{-1} ($X = Cl, Br, I$; $L = crown, cyclam$)	67
Table 12. The vibrational spectra of In_2X_6L below 500 cm^{-1} ($X = Cl, Br, I$; $L = crown, cyclam$)	72
Table 13. Comparison of ir frequencies (cm^{-1}) for CdX_2 and InX_2^+	73

Table 14. Some organoindium derivatives of dibenzo- 18-crown-6-ether	76
Table 15. Analytical results for some organoindium(III) compounds	81
Table 16. The revised infrared spectra of $\text{In}_2\text{X}_6^{2-}$ anions, as Bu_4N^+ salts	86
Table 17. Vibrational spectra of $\text{In}_2\text{X}_4\text{L}_2$	88
Table 18. Analytical results for some organoindium(III) compounds	99

LIST OF FIGURES

Figure 1. ^{115}In line widths as a function of solvent viscosity	35
Figure 2. ^{115}In chemical shift as a function of added $(\text{C}_6\text{H}_5)_4\text{PCl}$	42
Figure 3. ^{115}In chemical shift as a function of added $(\text{C}_6\text{H}_5)_4\text{PBr}$	44
Figure 4. Some typical ^{115}In -NMR spectra	50
Figure 5. ^{115}In chemical shifts as a function of total ligand electronegativity for $\text{InX}_n\text{Y}_{4-n}^-$ and InX_2YZ^- anions	55
Figure 6. Structure proposed for the adduct $\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$	90

TABLE OF ABBREVIATIONS

acac	acetylacetonate	s	strong
Bipy	bipyridine	sh	shoulder
br	broad	THF	tetrahydrofuran
Bu	butyl	TMED	N,N,N',N'-tetramethylethylene
crown	dibenzo-18-crown-6		diamine
	ether	TMS	tetramethylsilane
cyclam	1,4,8,11-tetraaza	vs	very strong
	cyclotetradecane	VSEPR	valence shell electron pair
Diox	1,4-dioxane		repulsion
DMSO	dimethylsulphoxide	vw	very weak
Et	ethyl	w	weak
HOMO	Highest occupied molecular orbital		
ir	infrared		
LUMO	lowest unoccupied molecular orbital		
m	medium		
Me	methyl		
NMR	nuclear magnetic resonance		
OAc	acetate		
Ph	phenyl		
Py	pyridine		
Ra	Raman		
RNBI	repulsive non bonded interaction		

GENERAL CONSIDERATIONS

A. INTRODUCTION

The element indium (atomic number 49) is the fourth member of Group IIIa of the Periodic Table. The investigation of the chemistry of this element has remained at a less intense level than for its Group IIa (Cd) or IVa (Sn) neighbours, or for the lighter members of its own Group (B or Al). Reasons for this lack of interest can be found in the low natural abundance of the metal, which occurs only in a proportion of 10^{-7} parts by weight in the terrestrial core, and also in the fact that no catalytic or wide synthetic applications have been discovered for its compounds. However, the metal does find widespread use in the electronic industry, as alloys with germanium (p-n junctions), phosphorus (high temperature transistors), and other Group Va elements (low temperature transistors). Other uses include low melting and dental alloys, and solders.

The electronic configuration of the element, $[\text{Kr}]4d^{10}5s^25p^1$, allows for oxidation states of I, II and III, the latter accounting for a large proportion of the known chemical combinations studied so far.

A detailed review of the coordination chemistry of indium is beyond the purpose of the present introduction, especially since these matters were extensively treated in

previous accounts (1, 2), which cover the current chemical literature until 1973. Also, the organic chemistry related to the element has been the subject of annual surveys (3) and a recent review (4). Other more recent evidence, especially reports dealing with low valent derivatives, are quoted and commented upon in the introduction of the relevant Chapters.

B. STRUCTURE AND BONDING IN INDIUM DERIVATIVES

Previous authors have commented on the lack of a theoretical model pertaining to the problem of bonding in non-transition elements (5). Different qualitative approaches to the description of the chemical bond in these elements have been proposed and used with varying degrees of success, depending on the problem at hand.

The valence-shell-electron-pair-repulsion theory (VSEPR) has been widely used. The fundamentals of this approach are that in a molecule repulsive interactions force bonding and lone electron pairs as far apart as possible, so that the geometry of the species to be analyzed can be predicted on this basis (6).

The repulsive-non-bonded-interaction model (RNBI) considers repulsions between ligands bonded to a metal atom as fundamental in determining the geometry of a species (7). A major problem found in the application of the latter concept is the assessment of the ligand size. Van der Waals repulsions have been used to define a steric angle,

considered as the principal region of steric influence of a donor atom. This model has successfully predicted geometry and stereochemistry in a number of Sn(IV) complexes (8). The same approach has been applied to indium(III) systems (1).

Useful as these models are, the scientist dealing with structural problems in indium chemistry is still in need of a theoretical, accurate and quantitative model of bonding. Moreover, the studies mentioned above only attempt the rationalization of features common to the chemistry of the trivalent state of the element. The lack of experimental information on the low oxidation states has prevented any extensive structural speculations concerning these derivatives.

C. THE PRESENT WORK

The fundamental problem, pursued throughout the different Chapters of this Dissertation, was the study of low valent indium compounds. Chapter 1 describes a series of reactions related to the first unambiguous indium(II) compounds, and Chapter 2 is a natural extension of the spectroscopic studies of the products of such reactions and related compounds. Some advances were made concerning compounds of indium(I). Chapter 3 deals with the preparation and spectroscopic properties of novel $[\text{In}(\text{crown})]^+$ and $[\text{In}(\text{cyclam})]^+$ cations. A limited number of adducts of

indium(II) were also made and studied, and these achievements form Chapter 4. Finally, Chapter 5 describes a series of unsuccessful attempts to make organoindium (I) and (II) compounds.

D. EXPERIMENTAL METHODS

This section is a brief description of the general experimental techniques used in the preparation and characterization of the materials quoted in the following Chapters. Since these manipulations involved rather common laboratory operations, the intention is to refer the reader to the original sources, when necessary. All operations involving air and/or moisture sensitive reagents were performed in a dry box, or using standard vacuum line techniques.

Purification of solvents. These methods have been extensively described (9). Aromatic solvents (benzene, toluene, mixture of isomeric xylenes), light petroleum ether (bp 40-60°) and diethyl ether were refluxed with sodium strip and benzophenone, and distilled from the blue ketyl formed. Acetone, acetonitrile, methylene chloride and chloroform were left in contact with calcium hydride until evolution of hydrogen ceased. Methanol and ethanol were distilled from the corresponding magnesium alkoxides.

Analytical Procedures. Halide analyses were done titrimetrically, by the Volhard method. In most cases,

the sample (0.05 to 0.1 g, depending on the halide content) was poured over excess silver nitrate solution and destroyed by slow addition of nitric acid at room temperature, in order to avoid loss of halide.

Indium analyses were done by atomic absorption, using standards made from indium metal and aqueous nitric acid. Typical sample sizes were 0.05 g, and readouts were of the order of $50 \times 10^{-3} \text{ gL}^{-1}$.

Sodium analyses were done by flame emission, using standards made from sodium chloride.

Carbon and Hydrogen analyses, when necessary, were done by Guelph Chemical Laboratories Limited, Guelph, Ontario.

Spectroscopy. Infrared spectra were recorded in a Beckman IR 12 instrument, between 4000 and 250 cm^{-1} . Cesium iodide pellets were used, unless stated otherwise.

Far infrared spectra were run in a Perkin Elmer 180 spectrometer, between 525 and 50 cm^{-1} , using suspensions of the solid samples in hydrocarbons, held between polyethylene plates.

^1H -NMR spectra were run on Varian 360 or JEOL C 60 instruments.

Raman spectra were run with a Spectraphysics 700 spectrometer. Solid samples were held in thin walled, sealed capillary glass tubes. Typical power outputs at the laser beam were 300 to 400 mW.

^{115}In -NMR were obtained with a Bruker CXP 100 variable frequency Fourier Transform spectrometer operating

at 19.72 MHz, with a magnetic field of 2.114 Tesla. The instrument was externally locked to the deuterium resonance of D_2O . All samples were run as solutions (approximately 3 mL volumes) in 1 cm o.d. tubes, at a temperature of 27°C, unless stated otherwise.

-Other Instrumentation. Conductivity measurements were done using a Phillips PR 9501 conductivity meter. Cell constants were usually 0.1 cm^{-1} .

Magnetic susceptibilities were measured with a Gouy balance (Newport Instruments).

Preparative, starting materials. Indium trichloride was prepared from the reaction of indium metal (Alfa, tear drop) heated to its melting point, and chlorine gas (10).

Indium tribromide: the procedure was essentially the same as for the trichloride, except that a stream of nitrogen saturated with bromine vapours was admitted to the system, instead of chlorine.

Indium triiodide was made from the metal and iodine in boiling xylenes (11).

Indium monohalides (chloride, bromide and iodide) were made by reduction of the appropriate trihalide with indium metal, in sealed tubes (12). Alternatively, the bromide and iodide were made by the disproportionation of the indium dihalides with a suitable base, generally diethyl ether (11) or ethanol.

Indium dihalides (chloride, bromide, iodide) were prepared from the corresponding trihalides and monohalides

in refluxing xylenes (11).

Hexahalogenodiindate(II) compounds were obtained as tetra-n-butylammonium salts from the reaction of the corresponding indium dihalides and the tetraalkylammonium halide in refluxing xylenes (13). The materials were purified by slow crystallization from acetonitrile and diethyl ether.

Methylindium diiodide was made from indium(I) iodide and methyl iodide (14). Irradiation with a 200 W lamp resulted in fast (1 hr) rates of reaction.

Dimethylindium iodide was obtained from indium trichloride, lithium iodide and methyllithium in diethyl ether (15).

Dimethylindium chloride and trimethylindium were made from indium trichloride and different proportions of methyllithium in diethyl ether (15).

Triphenylindium was prepared by the reaction of diphenylmercury and indium metal, in a sealed tube (16).

Diphenylindium iodide was obtained from the reaction of triphenylindium and iodine in benzene (17).

Cyclopentadienylindium(I) was made from indium trichloride and cyclopentadienylsodium in diethyl ether (18), or by the procedure described in Chapter 5.

Dihaloindate(I) anions were obtained as the tetraethylammonium salts from the reaction of cyclopentadienylindium(I), hydrogen halide and tetraethylammonium halide (19).

Indium(I) tetrachloroaluminate(III) was made from indium(I) chloride and aluminum trichloride in benzene (20).

Pentachloroindate(III), hexachloroindate(III) and tetrahalogenoindate(III) compounds were made from the reaction of the appropriate tetraalkylammonium salts and indium trihalides (21).

Tris-cyclopentadienylindium(III) was made from indium trichloride and cyclopentadienyllithium in diethyl ether (22).

CHAPTER 1.

THE PREPARATION AND VIBRATIONAL SPECTRA OF THE InX_3Y^- , InX_2Y_2^- AND MeInX_3^- SPECIES ($\text{X} \neq \text{Y} = \text{Cl}, \text{Br}, \text{I}$).

1.1 INTRODUCTION.

This Chapter deals with some of the chemical reactions of the first unambiguous indium(II) complexes, and with the properties of the products of these reactions. The preparation of the tetra-n-butylammonium salts of the hexahalogenodiiindate(II) anions was reported by Tuck *et al.* (13). Vibrational spectroscopy and some simplified force constant calculations showed that such species contain an indium-indium bond linking two InX_3^- units (13), in a structure analogous to that established in the x-ray diffraction study of $(\text{Me}_4\text{N})_2[\text{Ga}_2\text{Cl}_6]$ (23).

In this context, one obvious reaction is oxidation, in which one might expect cleavage of the indium-indium bond to give X_3InY^- compounds. By way of a preliminary study of the generality of such reactions, the oxidation of all three $\text{In}_2\text{X}_6^{2-}$ anions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with other halogens (Y_2) in benzene to give the anionic mixed halogeno complexes InX_3Y^- was studied.

A set of related experiments involved the oxidative addition of halogens Y_2 to the anions InX_2^- ($\text{X} \neq \text{Y} = \text{as before}$). These latter materials were prepared as the tetraethylammonium salts and characterized by vibrational spectroscopy, the

conclusion being that the structure of the anions in the solid involves monomeric species of C_{2v} symmetry (19). Oxidation of the species InX_2^- with halogens Y_2 led to complexes formulated as $InX_2Y_2^-$.

There have been no previous reports on the preparation or properties of such mixed halide complexes of indium, but several anionic complexes in which thallium(III) is bonded to two different halides have been reported. Preparative work (24-26), vibrational spectroscopy (25-27), electronic spectroscopy and x-ray powder methods (28) have established the existence of these mononuclear complexes, although there is some dispute as to whether or not dissociation in solution gives rise to mixtures of the appropriate TlX_4^- and TlY_4^- anions (27, 28).

Other experiments of cleavage of the metal-metal bond in the hexahalogenodiindate(II) anions involved methyl halides. These experiments afforded the tetrahaloindate(III) and methyltrihaloindate(III) anions. The preparation of the latter species was recently claimed through the electrochemical oxidation of a sacrificial indium electrode (29).

1.2 EXPERIMENTAL.

(a) $InCl_3I^-$, $InBr_3I^-$, $InCl_3Br^-$, InI_3Br^- , $InCl_2I_2^-$ and $InBr_2I_2^-$. Weighed quantities (approx. 2 mMol) of bromine or iodine were dissolved in benzene (50 mL), the solution heated to boiling and the calculated amount of the

appropriate indium salt added in small portions over about 5 min. The colour of the halogen discharged progressively during the addition, and the final colourless solution was allowed to cool to room temperature, when a brownish oil settled out. The benzene layer was decanted and the oil taken up in hot ethanol (20 mL): the solution was filtered hot, and allowed to crystallize on cooling.

(b) InBr_3Cl^- , InI_3Cl^- and $\text{InBr}_2\text{Cl}_2^-$. A solution of chlorine in benzene was prepared, and the concentration determined titrimetrically with sodium thiosulphate after addition of excess potassium iodide. Calculated amounts of the corresponding indium salts were then added to approx. 50 mL of a solution containing 2-4 mMol of molecular chlorine at room temperature, and the product isolated as before.

The order of addition of the reagents was found to be critically important, since if one adds a halogen Y_2 to a suspension of $\text{In}_2\text{X}_6^{2-}$ in benzene, precipitation of the Y_2X^- salt occurs more quickly than the redox reaction. This was demonstrated specifically in the simplest case, namely $\text{In}_2\text{I}_6^{2-} + \text{I}_2$, when the precipitated ammonium salt of the I_3^- anion was collected and identified. The significance of this result in terms of the reaction mechanism is discussed later.

The procedure described gave yields of crystalline products in the order of 60 to 80%. Analytical results and uncorrected melting points are given in Table 1.

Table 1. Melting points and analytical results for
 $[(C_4H_9)_4N]InX_3Y$ and $[(C_2H_5)_4N]InX_2Y_2$ salts

Anion	Melting pt. (°C)	Found(%)		Required(%)	
		In	Halogen (a)	In	Halogen (a)
$InCl_3Br^-$	128	21.0	34.2	21.1	34.3
$InCl_3I^-$	109 - 111	19.3	39.9	19.4	39.5
$InBr_3Cl^-$	128 - 130	17.9	43.3	18.2	43.5
$InBr_3I^-$	118 - 120	15.6	50.5	15.9	50.7
InI_3Cl^-	122 - 124	14.7	53.6	14.9	53.8
InI_3Br^-	125	14.1	56.3	14.0	56.3
$InCl_2Br_2^-$	288	24.5	48.3	24.1	48.5
$InCl_2I_2^-$	246	20.2	57.1	20.2	57.0
$InBr_2I_2^-$	289	17.4	63.0	17.4	62.8

(a) Expressed as $\%(X + Y)$ in each case..

(c) MeInCl_3^- , MeInBr_3^- and MeInI_3^- . Approximately 2 mmol of the appropriate hexahalogenodiindate(II) salt was suspended in benzene (30 mL) and the suspension frozen to liquid nitrogen temperature. An excess (two to threefold) of the methyl halide was condensed, and the mixture allowed to warm up to room temperature. After four to five hours of stirring the resulting heavy oil was allowed to settle and the solvent was decanted. The oils were treated with petroleum ether (bp 40 to 60°) to give yellow powders, which were taken up in acetonitrile (15 mL). After filtering minute amounts of insoluble residues, the solutions were treated with diethyl ether added dropwise until the cloudiness persisted. At this stage, the solutions were left in the freezer overnight, whereupon white crystals of tetrahalogenoindate(III) were separated from the solution. The latter was evaporated to dryness to yield impure methyltrihaloindate(III) salts. Three or more recrystallizations from the same solvent system gave materials of acceptable analytical purity (Table 2) in 50 to 60% yield according to the stoichiometry assumed.

(d) Experiments in which the salts $(\text{Bu}_4\text{N})_2[\text{In}_2\text{X}_6]$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) were added to benzene solutions containing equimolar amounts of dimethyldisulfide, MeS-SMe , yielded white amorphous materials. The atomic compositions, as revealed by analyses, indicated ratios of halogen/metal between 3 and 4. Repeated crystallizations from ethanol

Table 2. Analytical results for the $[(C_4H_9)_4N]MeInX_3$ salts.

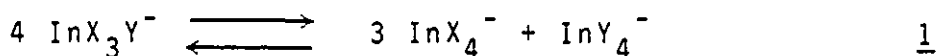
Anion	Found(%)		Required(%)	
	In	Halogen	In	Halogen
$MeInCl_3^-$	24.2	22.3	24.0	22.2
$MeInBr_3^-$	19.0	38.8	18.8	39.2
$MeInI_3^-$	15.5	51.0	15.3	50.6

failed to afford materials of sensible compositions. Infra-red spectra of these materials below 500 cm^{-1} were consistent with the presence of InX_4^- (X as before) plus other, not identified, species. These experiments were not pursued.

1.3 THE CLEAVAGE OF THE INDIUM-INDIUM BOND.

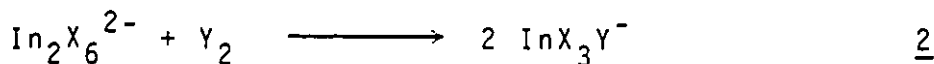
The preparation of the mixed ligand complexes InX_3Y^- and InX_2Y_2^- from indium(II) and (I) starting materials confirm the view expressed earlier (30) that such low valent compounds do indeed permit syntheses which cannot be readily carried out with indium(III) compounds.

The vibrational spectra, discussed below and force constant calculations (31) show that the products are indeed the mononuclear mixed ligand species, and not mixtures of (say) $3\text{ InX}_4^- + \text{InY}_4^-$. It might appear that the experimental conditions prevent significant redistribution *via* equilibria of the type



but additional evidence from ^{115}In -NMR studies (cf. Chapter 2) demonstrates the existence of rearrangements processes in polar solvents, *via* extensive halogen exchange, so that the view expressed previously (32) on the crucial role played by the solvent when dealing with the coordination chemistry of indium(III), is again demonstrated.

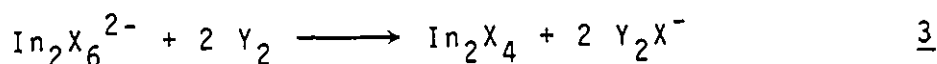
The reaction



describes the stoichiometry of the principal process, but

there are both experimental and theoretical reasons to believe that this process does not involve the flow of electrons from $\text{In}_2\text{X}_6^{2-}$ to Y_2 . Electron transfer in such a concerted reaction would be from the HOMO of the In_2 bond to the LUMO of the Y_2 , but the molecular orbitals involved in the In-In bond are of g symmetry, as opposed to the u symmetry of the LUMO level of Y_2 , implying that the reaction cannot be concerted. This argument is reinforced by the side products which are found in some cases (see below), but mainly by comparison to studies of the iodination of hexaorganoditin species, where kinetic data has been found consistent with a stepwise, ionic mechanism of rupture of the metal-metal bond (33-36).

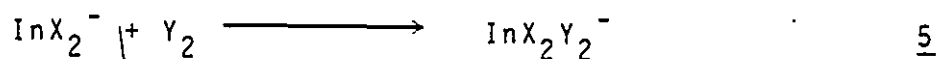
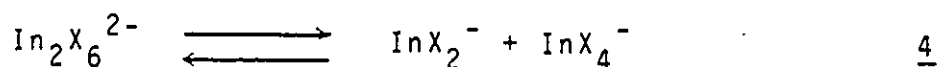
The precipitation of $\text{R}_4\text{N}^+ \text{X}_3^-$ salts when a solution of halogen is added to a suspension of the $\text{In}_2\text{X}_6^{2-}$ salts (see Experimental) points to the existence of a competing reaction, namely



The indium dihalides are known to be soluble in aromatic solvents (11), whereas X_3^- salts are demonstrably not. In fact, the preparative work involved the reverse procedure, namely the addition of solid $\text{In}_2\text{X}_6^{2-}$ salt to a solution of Y_2 , which is therefore present in local excess over the dissolving salt, and under these conditions the formation of InX_3Y^- will predominate. If the cleavage of the metal-metal bond in 2 is slow, or if the $\text{In} \dots \text{In} \dots \text{Y} \dots \text{Y}$ association is weak, then formation of the Y_2X^- species may

become significant.

One other important point relates to the formation of InX_2Y_2^- in those cases where the primary product is InX_3Y^- (cf. Section 1.4). The formation of these species was originally explained (31) by the sequence



Equilibrium 4 was proposed in earlier work to explain certain preparative results (13) and as with other equilibria involving indium halides, the equilibrium distribution is apparently solvent dependent. While it appears to lie strongly to the left in aromatic solvents at room temperature, small quantities of InX_2^- may well be present under the experimental conditions (80°C) and could lead to the formation of InX_2Y_2^- by reaction 5.

However, an alternative explanation in terms of halogen exchange, for which the ^{115}In -NMR results seem to give ample evidence, is also likely. This point is more comprehensively discussed in Chapter 2.

In summary then, the reactions in the $\text{In}_2\text{X}_6^{2-}$ systems are more complex than initially expected, but the analytical results (Table 1) and spectra show that the impurities are present in only small quantities. The reactions of InX_2^- , on the other hand, are apparently straightforward addition reactions, since no impurities are detected except in the case of $\text{InCl}_2^-/\text{I}_2$ (see below).

The reactions involving alkyl halides as oxidizing agents are simpler, from the point of view of the products involved, and they require little comment. It should be pointed out that materials containing the MeInCl_3^- anion were also reported in reactions of alkylation of pentachlorometal(V), MCl_5 ($\text{M} = \text{As}, \text{Sb}$), with dimethylindium chloride (37).

1.4 THE VIBRATIONAL SPECTRA OF THE InX_3Y^- ANIONS.

The vibrational representation of an InX_3Y species is $3 A_1 + 3 E$. The three A_1 modes are designated as $\nu_s(\text{InX}_3)$, $\nu_s(\text{InY})$ and the symmetric deformation δ_s , while the three E modes are $\nu_d(\text{InX}_3)$, $\delta_d(\text{InX}_3)$ (XInX scissors) and ω_d (wagging of the Y atom perpendicular to the InX_3 axis) (s = symmetric, d = degenerate).

The observed infrared and Raman spectra of the various InX_3Y^- anions are given in Table 3. The Table also lists the various bands not assignable to these anions (see below). It is as well to point out that in this Table there are some ambiguities, exemplified by the fact that ν_4 is the degenerate InCl stretch in InCl_3Br^- and InCl_3I^- , the degenerate InBr stretch in InBr_3Cl^- and InBr_3I^- , and the degenerate InI stretch in InI_3Cl^- and InI_3Br^- . The assignments have been made by comparing anions with common InX_3 and InY groups, and with the established assignments for InX_4^- (38, 41).

Table 3. The vibrational spectra of InX_3Y^- anions (in cm^{-1})

Assignment	(a) InCl_3Br^-	(b) InCl_3I^-	(c) InBr_3Cl^-	(d) InBr_3I^-	(e) InI_3Cl^-	(f) InI_3Br^-		
A_1	E	E	E	E	E	E		
ν_1	320s,sh 237ms 228ms 218m	320vs 258w 226s	315m,sh 185m	320s 184s 206s	318m 197s	325s 194vs 191ms	312m 305mw 216s	214m
ν_2								
ν_3								
ν_4								
ν_5								
ν_6								
Un- assigned (see text)								

In general, the far infrared spectra of the InX_3Y^- and InX_2Y_2^- species show broad bands, and the deformation bands in the region of 70 cm^{-1} are partially obscured by the polyethylene band at this frequency. The Raman spectra confirm the infrared stretching frequencies, but again some of the deformation modes near the exciting line are poorly defined. Fortunately, sufficient features are unambiguously established to show that the compounds are indeed salts of (say) InX_3Y^- anions. In the subsequent analysis, the anions are assumed to be sufficiently separated by the large cations that intermolecular coupling of vibrational motions can be safely ignored. Reasonable assignments can then be made on the assumption that local C_{3v} symmetry is operative for the InX_3Y^- species.

InCl_3Br^- : The assigned frequencies are given in Table 3(a). The InCl stretching modes ν_d and ν_s are straightforwardly assigned to 330 and 320 cm^{-1} respectively. Three bands at 237 , 228 and 218 cm^{-1} are observed in the expected region of $\nu_5(\text{InBr})$, instead of the predicted singlet; it is suggested that this is due to Fermi resonance between $2\nu_3$ and/or $2\nu_5$, and the fundamental is assigned to the average value of 228 cm^{-1} . The degenerate and symmetric $\delta(\text{ClInCl})$ bending modes are placed at 113 and 103 cm^{-1} respectively, corresponding to δ_d in InCl_4^- at 112 cm^{-1} , leaving the ClInBr bend to be assigned to a weak feature at 80 cm^{-1} .

InCl_3I^- : The modes assigned to the InCl_3 moiety (Table 3 (b)) are almost unchanged from those in InCl_3Br^- . The InI symmetric stretch, which occurs with medium intensity in the infrared and is strong in the Raman spectrum, is placed at 185 cm^{-1} . The degenerate ClInI deformation is predicted to be close to 70 cm^{-1} and a weak band is apparent in the spectra at 65 cm^{-1} . Weak features in the ir spectrum at 192 and 170 cm^{-1} cannot be accommodated in this scheme, and it is believed that these bands indicate the presence of small quantities of $\text{InCl}_2\text{I}_2^- + \text{InCl}_4^-$ in the product. These are the only vibrations in such a mixture which would not be coincident, or nearly so, with the bands of InCl_3I^- . The routes by which these impurities could have been formed are better discussed on the light of the ^{115}In -NMR experiments (cf. Section 2.7).

InI_3Cl^- and InI_3Br^- : For these species, in which the InX_3 group involves the heaviest halogen (Table 3, (a) and (b)), the assignments to fundamentals which correspond to motions of the InI_3 group are very similar in both cases. The symmetric InI stretches are at 137 and 149 cm^{-1} and the degenerate stretches are located at 186 and 185 cm^{-1} respectively. The degenerate bending mode, $\delta(\text{IInI})$ is at 45 cm^{-1} in both molecules, while the corresponding symmetric modes are slightly higher, at 65 and 61 cm^{-1} in the chloride and bromide respectively. The ClInI deformation, at 70 cm^{-1} , is higher than the corresponding BrInI mode, as expected on the bases of relative mass. In both systems, high

energy shoulders suggest some slight contamination of the product by the appropriate InX_2Y_2^- anion (see discussion below in terms of InBr_3I^-).

InBr_3Cl^- : The assignment of the spectrum is relatively straightforward, based on comparison with the other mixed species and with InBr_4^- .

InBr_3I^- : There are more spectral features than can be accounted for in terms of this anion alone. The assignments in Table 3(d) were made by comparison with other InX_3Y^- anions.

In this way, the degenerate and symmetric $\nu(\text{InBr}_3)$ stretches are placed at 230 and 194 cm^{-1} , and the degenerate $\delta(\text{BrInBr})$ at 76 cm^{-1} (cf. analogous bands at 225, 205 and ca. 70 cm^{-1} in InBr_3Cl^-). The bands at 60 and 50 cm^{-1} present in both infrared and Raman spectra are assigned to ν_3 and ν_6 respectively. This leaves the InI stretching mode to be assigned, with possible candidates being the features at 168, 156 and 139 cm^{-1} , all in the region predicted for this vibration. The most intense band at 168 cm^{-1} is assigned to $\nu(\text{InI})$.

It is believed that the extra bands are due to the presence of $\text{InBr}_2\text{I}_2^-$ (cf. discussion in Section 2.7). One would then expect to see the various vibrations of $\text{InBr}_2\text{I}_2^-$ and InBr_4^- . Most of the spectral features of $\text{InBr}_2\text{I}_2^-$ are coincident, or nearly so, with those of InBr_3I^- , with the exception of ν_3 (149 cm^{-1}), and there is indeed a strong

shoulder in the Raman spectrum of InBr_3I^- at 156 cm^{-1} ; the ν_7 band of $\text{InBr}_2\text{I}_2^-$ (188 cm^{-1}) would be masked by ν_1 of InBr_4^- (195 cm^{-1}). Similarly in the infrared, ν_3 of InBr_4^- (239 cm^{-1}) would be in the broad envelope centered at 230 cm^{-1} (ν_4 of InBr_3I^-).

1.5 THE VIBRATIONAL SPECTRA OF THE InX_2Y_2^- ANIONS.

The spectra of all the InX_2Y_2^- species ($X \neq Y = \text{Cl, Br, I}$) can be assigned on the basis of C_{2v} symmetry (Table 4). Eight of the nine fundamentals ($4A_1$, $2B_1$ and $2B_2$) are both Raman and infrared active while the A_2 mode is active only in the Raman mode. The assignments are made initially on the basis of group characteristics. Thus, the three vibrations characteristic of the InCl_2 moiety are readily identified. The strong infrared band to highest wave number is clearly the antisymmetric InCl_2 stretch at 328 cm^{-1} in $\text{InCl}_2\text{Br}_2^-$ and at 320 cm^{-1} in $\text{InCl}_2\text{I}_2^-$ (see Table 4, (a) and (b)), with the corresponding distinct bands in the Raman spectra at 320 and 313 cm^{-1} being the symmetric ν_{a1} (InCl_2) modes. The symmetric δ_{a1} (InCl_2) bend is undoubtedly the band near 105 cm^{-1} in both spectra. The corresponding three characteristic vibrations for the InBr_2 group can similarly be identified as the ν_b (InBr_2) mode at 236 and 229 cm^{-1} , the ν_{a1} (InBr_2) mode at 206 and 215 cm^{-1} and the δ_{a1} (InBr_2) mode at 74 and 77 cm^{-1} respectively, in $\text{InCl}_2\text{Br}_2^-$ and $\text{InBr}_2\text{I}_2^-$ (Table 4, (a) and (c)). Furthermore, the characteristic bands of the InI_2 group show up

Table 4. The vibrational spectra of InX_2Y_2^- anions
(in cm^{-1})

Assignment		(a) $\text{InCl}_2\text{Br}_2^-$		(b) $\text{InCl}_2\text{I}_2^-$		(c) $\text{InBr}_2\text{I}_2^-$	
A_1	B	ir	Ra	ir	Ra	ir	Ra
ν_1		325sh	320m	310sh	313s	215m	219m
ν_2		210m	206m	167mv	167s	149vw	149vs
ν_3		105m		105m		77vw	
ν_4		n.a. (*)		n.a. (*)		n.a. (*)	
ν_5		74w		50m		48sh	
	ν_6	328s	328sh	322s	320sh	229s	230sh
	ν_7	236vs	230sh	187m	184s	187s	188s
	ν_8	94sh		90sh		65sh	
	ν_9	82m	80ms	80sh		51m	

(*) A_2 ir inactive mode

as the $\nu_b(\text{InI}_2)$ mode at 187 cm^{-1} (in both cases), the $\nu_{a1}(\text{InI}_2)$ at 167 and 149 cm^{-1} , and the $\delta_{a1}(\text{InI}_2)$ mode at 50 and 48 cm^{-1} respectively in $\text{InCl}_2\text{I}_2^-$ and $\text{InBr}_2\text{I}_2^-$. The remaining three modes, involving the motion of two different halides in each InX_2Y_2^- ion include the torsional mode, which is only Raman active and not observed in the infrared spectra. The two remaining modes δ_{b1} and δ_{b2} are assigned to the peak in both the Raman and infrared spectra of $\text{InCl}_2\text{Br}_2^-$ at 80 cm^{-1} and to a shoulder at 94 cm^{-1} in the infrared spectrum respectively. The corresponding modes in $\text{InCl}_2\text{I}_2^-$ are assigned to two shoulders at 80 and 90 cm^{-1} , and in $\text{InBr}_2\text{I}_2^-$ to a distinct peak at 51 and a shoulder at 65 cm^{-1} .

In $\text{InCl}_2\text{I}_2^-$, there is a weak Raman and infrared feature at 155 cm^{-1} , which might be evidence of I_3^- as a low level impurity (cf. ν_3 of I_3^- at approx. 150 cm^{-1} (42)). It is worth noting that the problems with impurity bands arise most closely in those systems where iodine is the oxidizing agent. Such problems apart, the vibrational spectral assignments appear to be unambiguous and confirm the conclusions of the preparative work.

1.6 THE MeInX_3^- ANIONS.

The vibrational analysis of these species follows the same general lines as in the case of the tetrahaloindates of C_{3v} symmetry described in Section 1.4. Complete vibrational data is available only for the Cl derivative.

In the case of the Br and I species, the low energies at which the deformation modes are found, and the poor quality of the Raman spectra prevent any detailed analysis of these features.

Perhaps the band which is most easily assigned in the spectra is $\nu_s(\text{InC})$, at 522, 500 and 496 cm^{-1} in the chloro, bromo and iodo derivatives respectively (see Table 5). Also discernible in all three cases are $\nu_d(\text{InX}_3)$ and $\nu_s(\text{InX}_3)$ at 300 and 288 cm^{-1} for MeInCl_3^- , 210 and 200 cm^{-1} for MeInBr_3^- , and 165 and 152 cm^{-1} for MeInI_3^- . The rest of the spectral data for MeInCl_3^- differs from the one published by Widler et al. in their study of the species

$\text{Me}_4\text{M}^+ \text{MeInCl}_3^-$ (M = As, Sb) (37). No infrared or Raman components of the 110 cm^{-1} feature claimed by these authors were found in the spectra of the tetra-n-butylammonium salts reported here. Moreover, the mode assigned as $\delta(\text{SbCl}_4)$ at 214 cm^{-1} (37) can be correlated to the strong infrared feature at 206 cm^{-1} in the present spectra. On this basis, the following assignments are proposed as tentative:

$\delta_d(\text{InCl}_3)$ at 206 cm^{-1} , $\delta_s(\text{InCl}_3)$ at 130 cm^{-1} and $\delta(\text{ClInCl})$ at 120 cm^{-1} .

This information shows that the products of the reaction between the hexahalogenodiindate(II) anions and the appropriate methyl halides are the tetrahaloindate(III) and the alkyltrihaloindate(III) anions. The preparation of the latter is then possible through a number of alternative routes:

Table 5. The vibrational spectra of MeInX_3^- anions
(in cm^{-1})

Assignment	MeInCl_3^- ir Ra	MeInBr_3^- ir Ra	MeInI_3^- ir Ra
$\nu_s(\text{InC})(A_1)$	522s 520w	500s 501w	496s 498w
$\nu_s(\text{InX}_3)(A_1)$	300s,sh 298s	210vs 210m	165s 166m
$\nu_d(\text{InX}_3)(E)$	288vs 288w	200s,sh 198m	152m 150w
$\delta_d(\text{InX}_3)(E)$	206s 205w	85m	
$\delta_s(\text{InX}_3)(A_1)$	130m,sh 130w		
$\delta(\text{CInX})(E)$	120s 118w		

- (a) This method.
- (b) Reaction of MeInX_2 and tetraalkylammonium halides (43).
- (c) Electrochemical oxidation of indium metal in the presence of alkyl halides and the appropriate tetraalkylammonium salt (29).
- (d) Alkylation of pentachlorometal(V) with dimethylindium chloride (37).

1.7 CONCLUSIONS.

The principal mode of interaction of the hexahalogenodiindate(II) anions with molecular halogens and methyl halides involves oxidative cleavage of the metal-metal bond to afford products which, from a formal point of view, can be regarded as arising from the homolytic fission of the concerned bonds.

CHAPTER 2

^{115}In -NMR-STUDIES OF ANIONIC INDIUM SPECIES IN NONAQUEOUS SOLUTION

2.1 INTRODUCTION.

The solution chemistry of the complexes of indium, and especially those involving halide ligands, has been the subject of some speculation, much of it based on evidence which is at best indirect. The results of both spectroscopic and preparative work have been interpreted in terms of the various species presumed to be present, but as pointed out elsewhere, the preparative evidence must be treated with caution in this respect (1, 2). Of the spectroscopic techniques available at the present time, nuclear magnetic resonance offers the distinct possibility of obtaining information not otherwise available. Both ^{115}In (95.75% abundant) and ^{113}In (4.28%) have high nuclear spins ($I = 9/2$) which render the technique intrinsically difficult, but previous workers have shown that useful information can be obtained.

Line broadening of the resonances in aqueous solutions of $\text{In}(\text{ClO}_4)_3$ and $\text{In}(\text{NO}_3)_3$ has been observed and explained in terms of asymmetry of the molecular environment, viscosity of the solvating media, or chemical exchange (44). At low temperatures, the exchange process can be conveniently slowed down, so that separate ^{115}In resonances can be

observed for the limiting structures InX_4^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{In}(\text{H}_2\text{O})_6^{3+}$ (45). Other studies related to the tetrahaloindate(III) series (46) are referred to in section 2.4. The literature on this and related topics has been reviewed by Hinton and Briggs (47).

^{115}In -NMR studies of a number of anionic complexes and related species in nonaqueous solutions were carried out during the present work. As reported previously, the absorption bands are broad, but the chemical shifts due to ligand substitution, changes in coordination number, etc. are sufficiently large to minimize this factor. The spectral results serve both to reinforce earlier work on the solution chemistry of some of the complexes involved, and to provide new information on the behaviour of others.

2.2 ^{115}In -NMR SPECTROSCOPY. GENERAL.

As with other elements, changes in molecular structure and environment may affect both resonance frequency and line width in ^{115}In -NMR spectroscopy. In particular, the symmetry of the electronic environment at the indium nucleus defines the magnitude of the electric field gradient, whose interaction with the nuclear quadrupole governs the relaxation times, and hence the spectral line widths. The narrowest lines are, therefore, to be expected in tetrahedral or octahedral species, narrow in this context implying half-widths ($\Delta H_{1/2}$) of less than 1000 Hz. In such cases, line broadening on the addition of (say) halide ions to the

solution may indicate the onset of some exchange reaction, although specific ion pair formation may also cause similar effects (cf. Section 2.4).

Previous investigators have reported chemical shifts (δ) in terms of a standard acidified aqueous solution of indium(III) perchlorate. The results in the Chapter are referred to a zero corresponding to the ^{115}In resonance of a 0.5 M solution of InCl_4^- in dichloromethane. The difference of 441 ppm between InCl_4^- and $[\text{In}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ found in the present work is close to the chemical shift of 430 ± 15 ppm for InCl_4^- in various nonaqueous solvents relative to $[\text{In}(\text{H}_2\text{O})_6]^{3+}$ in water (cf. reference (47) for a compilation of previous results).

2.3 SOLVENT AND CONCENTRATION EFFECTS.

The tetrahedral structure of the InX_4^- anions, predicted as the result of vibrational studies, has been confirmed by x-ray diffraction in the case of InCl_4^- (48), InBr_4^- (49) and InI_4^- (50). Such species have been shown to give narrow line spectra in aqueous as well as organic solvent solutions, with chemical shifts of -440, -180 and 580 ppm (chloride, bromide and iodide respectively) from $\text{In}(\text{H}_2\text{O})_6^{3+}$. As a preliminary to an investigation of the spectra of other complexes, it was demonstrated that changes in solute concentration or solvent have only a slight effect on the resonance frequency. Table 6 shows that, for a series of solvents, and for concentrations over

Table 6. Concentration and solvent dependence of ^{115}In resonance of $[(\text{C}_6\text{H}_5)_4\text{P}]\cdot[\text{InCl}_4]$ at 27°C .

Solvent	$[(\text{C}_6\text{H}_5)_4\text{P}]\cdot[\text{InCl}_4]$ concn. (M)	(ppm)(a)	$\Delta H_{1/2}$ (Hz)(b)
CH_2Cl_2	0.1 - 0.5	0	365
Acetone	0.1	+3.9	183
CH_3CN	0.1	0	312
Tetrahydrofuran	0.1	-1.6	417
CHCl_3	0.1	-3.1	729
Methanol	0.1	very broad	

(a) ± 1 ppm

(b) ± 30 Hz

the range 0.1 to 0.5 M in dichloromethane, the frequency shifts are identical, within experimental error. Accordingly, in the latter parts of this Chapter, the frequencies of compounds in different solvents are compared without any correction factor.

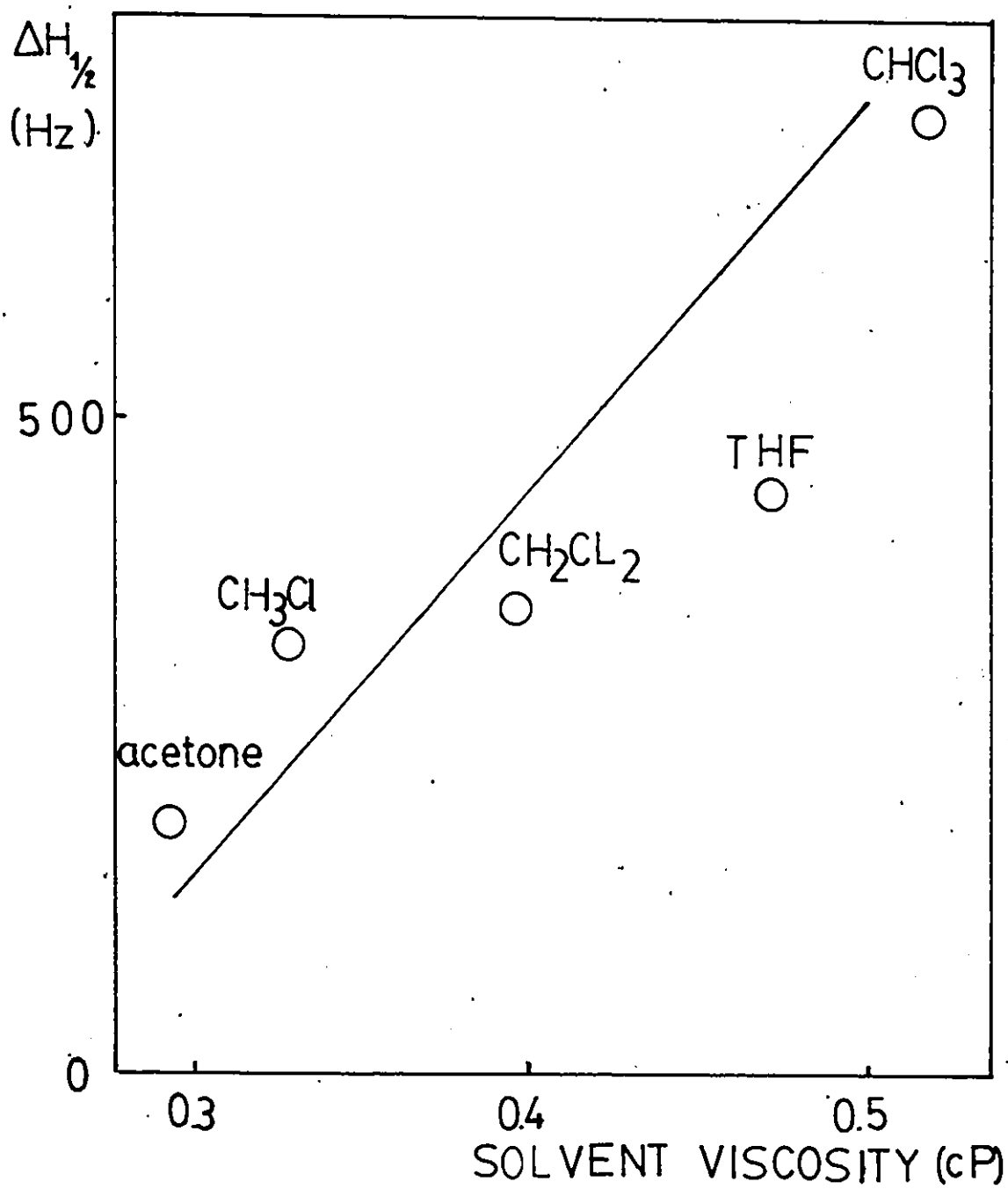
The solvent dependence of the line width deserves some comment, since the ΔH_q values range from approximately 200 to 800 Hz. The line width of the species InX_4^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), taken as a working example, is mainly determined by quadrupole relaxation, and can be expressed as a linear function of, *inter alia*, τ_c , the rotational correlation time. In a rigid sphere model, τ_c is given by $4\pi r^3 \eta / 3kT$, where r is the molecular radius and η is the viscosity of the solution (46).

Figure 1 shows a plot of the experimental line widths versus viscosity of the solution (assuming that one can use the available viscosities of the pure solvents, rather than those of the experimental solutions). The linear dependence, within the assumptions made, shows that a significant contribution to the line narrowing process must arise from molecular rotation in solution. No explanation is forthcoming for the deviation found in THF solution, where complexation and/or exchange are expected to cause broadening, rather than the observed narrowing (see Figure 1).

Figure 1 ^{115}In line width as a function of solvent
viscosity.

0.1M solutions of $[(\text{C}_6\text{H}_5)_4\text{P}] [\text{InCl}_4]$.

FIGURE 1



2.4 THE TETRAHALOGENOINDATE(III) ANIONS.

Table 7 shows the ^{115}In resonances of various species known from x-ray or spectroscopic studies to contain tetrahedral InX_4^- anions. We first note that each of the anions InCl_4^- , InBr_4^- and InI_4^- shows a relatively sharp single resonance, in keeping with the high symmetry. The chemical shift, δ , is defined as $(\nu - \nu_0/\nu_0) \cdot 10^6$ ppm, and the upfield shift in the order $\text{InCl}_4^- < \text{InBr}_4^- < \text{InI}_4^-$ then accords with the increasing electron density around the indium nucleus as the ligand electronegativity decreases along the series.

Previous studies reported a noticeable narrowing of the ^{115}In resonance with increasing molecular radius in the series InX_4^- (X as before). It was suggested that ion pairing of the tetrahedral indium species with the counter ion in solution causes additional fluctuation in the electric field gradient, and that this effect decreases down the series $\text{Cl} > \text{Br} > \text{I}$, accounting for the observed differences in line widths (46). The present results show such effect in solutions of $\text{Ph}_4\text{P}^+ \text{InX}_4^-$ (X = Cl, Br) in acetonitrile or methylene chloride. The observation cannot be extended to the InI_4^- salts, since the presence of different cations also causes sizable line width effects.

The three formally neutral compounds in Table 7 are all cases in which an ionic dimer formulation has been proposed. Thus for $\text{InI}_3 \cdot 2\text{DMSO}$, x-ray methods established

Table 7. ^{115}In resonances for InX_4^- salts, and related compounds, in non-aqueous solution

Compound	Solvent	Conc. (M)	(a) (ppm)	$\Delta H_{1/2}$ (b) (Hz)
$[(\text{C}_6\text{H}_5)_4\text{P}] [\text{InCl}_4]$	various	various	0	See Table 6
$[(\text{C}_6\text{H}_5)_4\text{P}] [\text{InBr}_4]$	CH_2Cl_2	0.1 - 0.5	-265	286
$[(\text{C}_6\text{H}_5)_4\text{P}] [\text{InBr}_4]$	CH_3CN	0.1	-258	182
$[(\text{C}_4\text{H}_9)_4\text{N}] [\text{InI}_4]$	CH_3CN	0.03	-989	250
$[(\text{C}_6\text{H}_5)_3\text{CH}_3\text{As}] [\text{InI}_4]$	CH_2Cl_2	0.1	-1010	433
$\text{InI}_3 \cdot 2\text{DMSO}$	acetone	0.075	-1013	450
$\text{InI}_3 \cdot 2\text{CH}_3\text{CN}$	acetone	0.075	-1013	1000
CH_3InI_2	CH_3CN	0.6	-1005	1120

(a) ± 1 ppm for InCl_4^- and InBr_4^- ; ± 5 ppm for iodide species

(b) ± 30 Hz

the structure $[\text{InI}_2(\text{DMSO})_4]^+ [\text{InI}_4]^-$, while vibrational spectroscopy indicates that the formulae of the other two compounds in the solid state are $[\text{InI}_2(\text{CH}_3\text{CN})_4]^+ [\text{InI}_4]^-$ (29) and $[(\text{CH}_3)_2\text{In}]^+ [\text{InI}_4]^-$ (14). In each case, the NMR results confirm the presence of the InI_4^- anion in solution. No resonance was observed for any of the cations in these systems. This may be the effect of either the molecular symmetry, which involves *cis*- $[\text{InI}_2\text{L}_4]^+$, or of ligand/solvent exchange. For the $[(\text{CH}_3)_2\text{In}]^+$ cation, solvation may well lead to the formation of $[(\text{CH}_3)_2\text{In}(\text{CH}_3\text{CN})_4]^+$ species in solution, again lowering the symmetry of the cation.

Finally, it is noted that InI_3 , which has the iodine bridged structure $\text{I}_2\text{InI}_2\text{InI}_2$ in the solid state and in non-donor solvents (51), also gives a resonance at -1031 ± 5 ppm from InCl_4^- ($\Delta H_{1/2}$ 1354 Hz) in methylene chloride. The formal charge apparently has little effect on the resonance frequency, given that both InI_4^- and In_2I_6 involve In(III) tetrahedrally bonded to iodine. No resonance was detected for solutions of either InCl_3 or InBr_3 in acetonitrile or dichloromethane.

2.5 HEXAHALOGENODIINDATE(II) ANIONS.

There is sufficient evidence in favour of an ethane-like staggered conformation for these anions in the solid state (cf. reference (13) and also Chapter 1). The ^{115}In -NMR of solutions of these materials in acetonitrile shows a single resonance in each case:

$[(C_4H_9)_4N]_2[In_2Cl_6]$	- 2 ppm	$\Delta H_{1/2}$ 500 Hz
$[(C_4H_9)_4N]_2[In_2Br_6]$	- 258 ppm	$\Delta H_{1/2}$ 330 Hz
$[(C_4H_9)_4N]_2[In_2I_6]$	- 989 ppm	$\Delta H_{1/2}$ 250 Hz

The chloride and iodide compounds were at formal concentrations of 0.1 M and the bromide at 0.05 M.

The resonances observed are almost identical in frequency to those found for the corresponding InX_4^- anions (cf. Table 7). This result finds a ready explanation in the previously proposed disproportionation equilibrium 4 (cf. Section 1.3). It is believed that the failure to observe resonances from $In_2X_6^{2-}$ or InX_2^- (for which a bent structure has been proposed) is due to the low symmetry of these species (13, 19).

The intensity of the InX_4^- peak in the spectra of $In_2Cl_6^{2-}$ was compared to that of a solution of InX_4^- of known concentration in the same solvent under identical instrument conditions, thus allowing an estimate of the concentration of each species in equilibrium 4 (Section 1.3) and hence of the equilibrium constants. We found $K \sim 0.02$ for the chloride and ~ 0.2 for the iodide in acetonitrile at 27°C, showing that the chloro compound is significantly more stable to disproportionation than is the iodide. This is in keeping with the previous spectroscopic and force constant analysis (13), which gave values of 0.63 and 0.24×10^{-5} dyn/cm for the indium-indium stretching force constants in the chloride and iodide systems respectively; this agreement

unfortunately reveals nothing as to the mechanism of rupture of the indium-indium bond of these anions in solution.

2.6 THE $\text{InX}_4^-/\text{X}^-$ SYSTEMS.

An investigation of the effect of halide excess on the ^{115}In resonance of the species InX_4^- was undertaken, in the belief that line broadening would give information on the details of the halogen exchange process. In fact, the most obvious effect involved changes in the chemical shift. These changes are shown in Figure 2 for $\text{X} = \text{Cl}$, and Figure 3 for $\text{X} = \text{Br}$. In both cases, the experimental limits were fixed by the solubility of the tetraphenylphosphonium salts in acetonitrile.

It should be noted first that for InI_4^- , the addition of $(\text{C}_6\text{H}_5)_4\text{PI}$ up to a threefold excess produced no change in either chemical shift (-1007 ± 1 ppm) or line width (150 ± 25 Hz) of the InI_4^- resonance. This is in keeping with previous studies (1) showing that the maximum coordination number for anionic iodoindium(III) species is four. The result also shows that changes in susceptibility, dielectric constant, etc. due to the addition of excess halide do not influence the ^{115}In chemical shift (cf. Tables 6 and 7) so that the changes observed in other systems ($\text{X} = \text{Cl}, \text{Br}$) can be discussed in this light.

For the $\text{InCl}_4^-/\text{Cl}^-$ system, the marked change in chemical shift indicates further complexing which may involve

Figure 2. ^{115}In chemical shift as a function of
added $(\text{C}_6\text{H}_5)_4\text{PCl}$.
Initial solution 0.1 M $[(\text{C}_6\text{H}_5)_4\text{P}] [\text{InCl}_4]$
in acetonitrile.

FIGURE 2

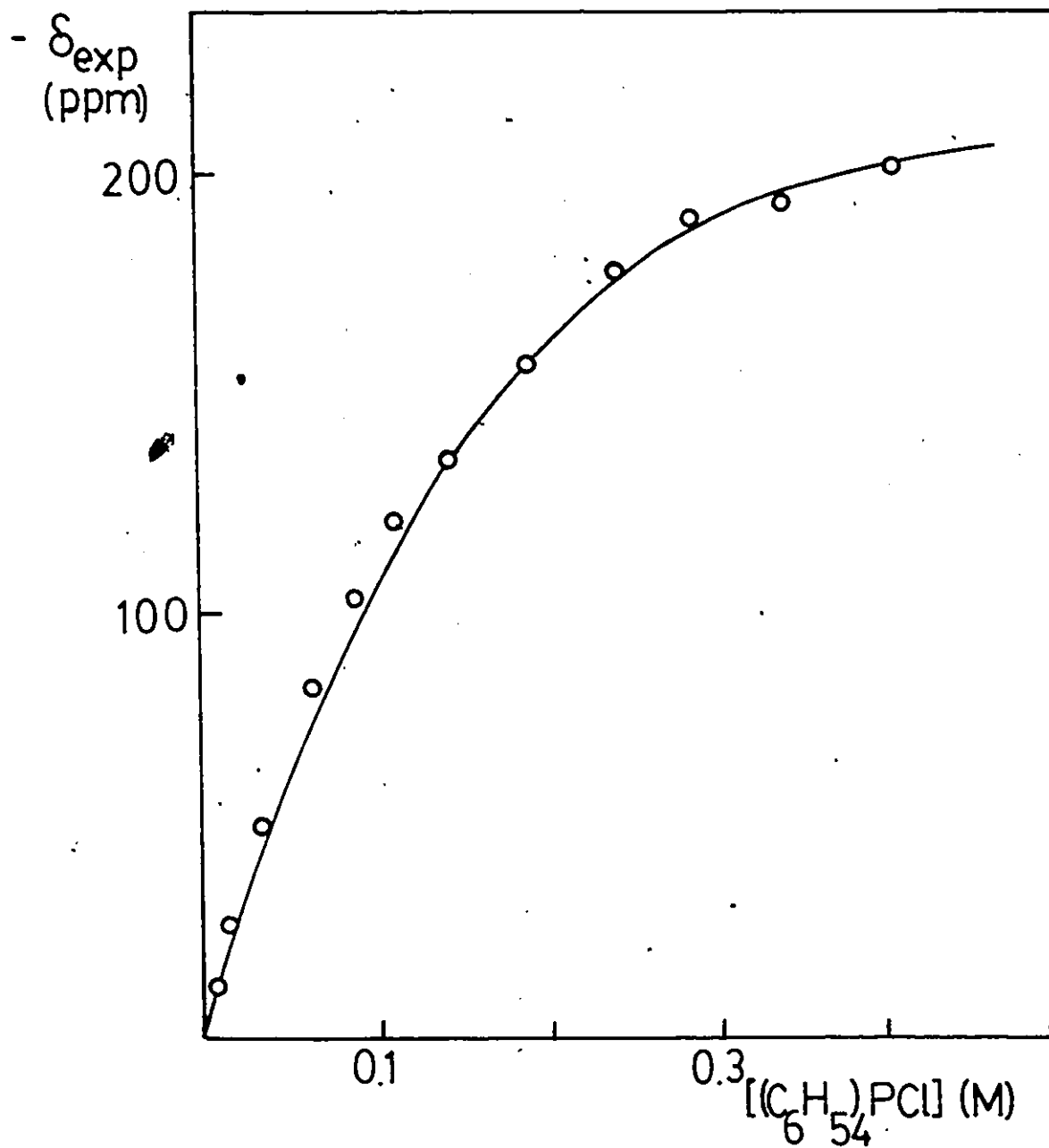
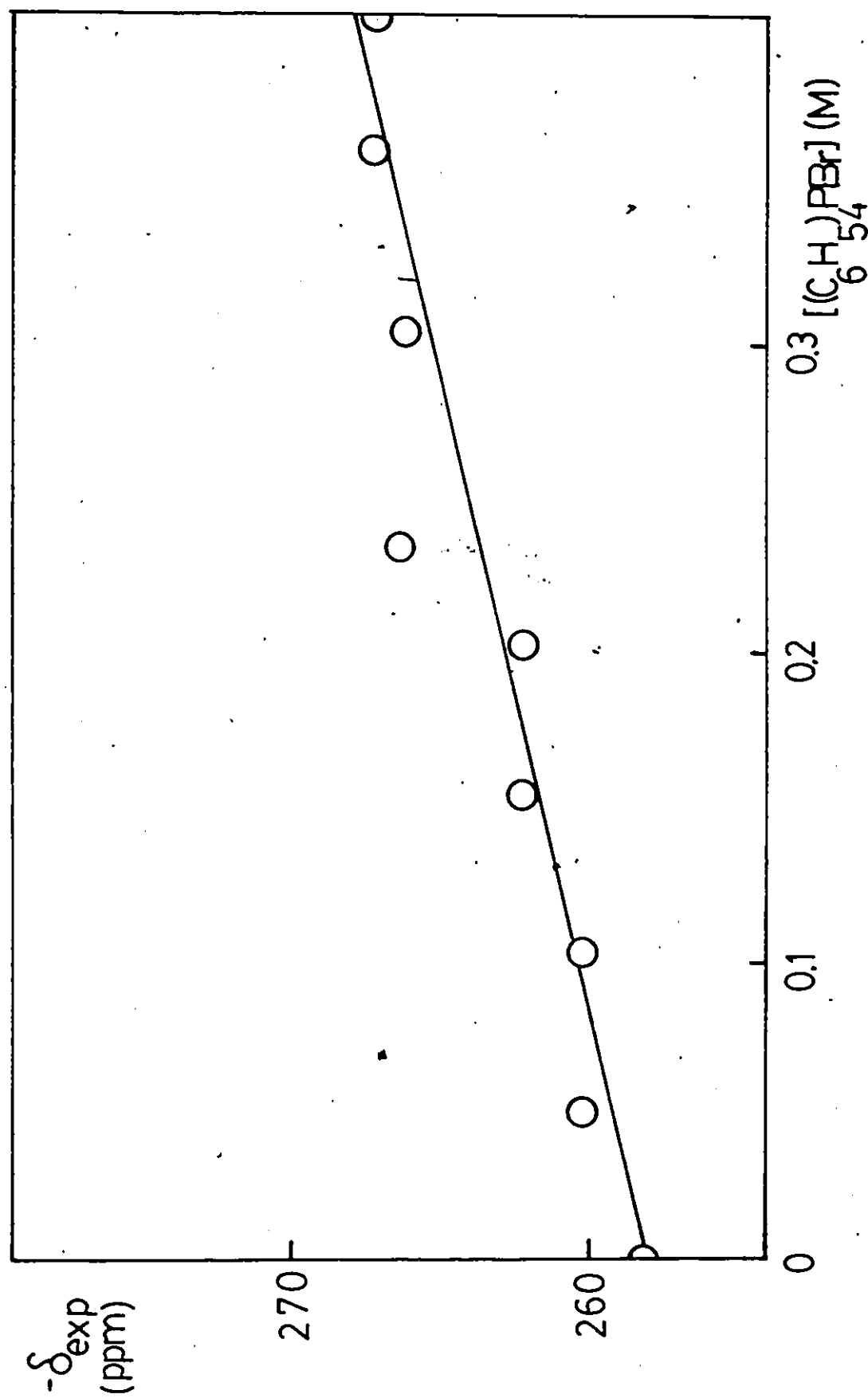
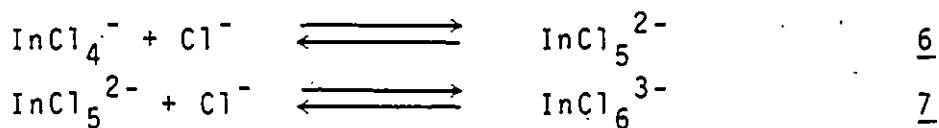


Figure 3. ^{115}In chemical shift as a function of added $(\text{C}_6\text{H}_5)_4\text{PBr}$.
Initial solution 0.1 M $[(\text{C}_6\text{H}_5)_4\text{P}][\text{InBr}_4]$
in acetonitrile.

FIGURE 3



one or both of the equilibria



Attempts to fit a calculated curve to the experimental points in Figure 2 considering equilibrium 6 only, were not successful. The analysis included then both simultaneous equilibria 6 and 7, for which the equilibrium constants K_5 and K_6 apply. The treatment initially assumed a chemical shift δ_6 for InCl_6^{3-} in the order of -220 ppm from InCl_4^- , and further assumed that $K_6 \ll K_5$. The best fit to the experimental results gives $\delta_5 = -115$ and $\delta_6 = -235$ ppm (each ± 5 ppm), and $K_5 = 350 \pm 100$, $K_6 = 10 \pm 3$, from which one derives the curve shown (Figure 2) fitting the experimental points satisfactorily (see Appendix A for details).

Both InCl_5^{2-} and InCl_6^{3-} anions have been identified previously. The pentachloroindate(III) anion is a rare example of a main group complex having C_{4v} symmetry in the solid state (52, 53) and equilibrium 6 was proposed earlier to explain experimental results involving the recrystallization of $[(C_2H_5)_4N]_2 [InCl_5]$ from non-aqueous solutions (21). For the thallium analogue $TlCl_5^{2-}$, spectroscopic studies (54) of solutions in nitromethane gave $K_5 = 0.2$, significantly smaller than that found above (for acetonitrile). The InCl_6^{3-} anion is also a known species, with the expected octahedral structure in the solid state (21, 55).

The $\text{InBr}_4^-/\text{Br}^-$ system shows evidence for the formation of complexes with coordination numbers higher than four, but because of the small changes in chemical shift, the results do not lend themselves to the above analysis.

The general conclusion is that K_5 goes in the order $\text{Cl} \gg \text{Br} \gg \text{I} = 0$, a result which parallels the preparative work (1, 21). In this context, it should be noted that the InBr_5^{2-} anion has not been stabilized in the solid state, although InBr_6^{3-} salts are known (21), and the experimental results in Figure 3 may reflect a similar difficulty in forming five-coordinate In(III)/Br anionic complexes in solution.

The chemical shifts for InCl_5^{2-} and InCl_6^{3-} deserve some comment. The effect of adding extra chloride ions to the coordination shell of In(III) is to produce changes in shielding similar to those of replacing chloride by bromide (cf. Table 7 and the discussion of $\text{InX}_n\text{Y}_{4-n}^-$ species in Section 2.7). Both situations represent potentially increased electron donation to the indium(III) ion as the number of chlorides increases, and/or the electronegativity of the ligand decreases. There are at present no experimental methods of separating these two effects, but it is worth noting that the present NMR results demonstrate such changes much more clearly than did earlier studies of x-ray photoelectron spectra of these anions in the solid state (56).

Table 9. Mean ^{115}In resonances for $\text{InX}_4\text{Y}_{4-n}^-$ Anions in Dichloromethane

	Anion	δ (ppm \pm 2%)
1	InCl_4^-	0
2	InCl_3Br^-	52
3	$\text{InCl}_2\text{Br}_2^-$	117
4	InClBr_3^-	187
5	InBr_4^-	264
6	InBr_3I^-	429
7	$\text{InBr}_2\text{I}_2^-$	616
8	InBrI_3^-	812
9	InI_4^-	1010
10	InCl_3I^-	190
11	$\text{InCl}_2\text{I}_2^-$	429
12	InClI_3^-	706
13	$\text{InCl}_2\text{BrI}^-$	258 (a)
14	$\text{InClBr}_2\text{I}^-$	337
15	InClBrI_2^-	513

(a) Estimated: see text

2.7 MIXED HALOGENO SPECIES InX_3Y^- , InX_2Y_2^- AND InX_2YZ^- .

The previous Chapter described the preparation of anionic indium(III) complexes of the type InX_3Y^- and InX_2Y_2^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The vibrational spectra (Chapter 1) and force constant calculations (31) supported the structural assignment of these anions as displaying C_{3v} or C_{2v} symmetry, and this has subsequently been confirmed in the case of InCl_3Br^- and InBr_3Cl^- by x-ray crystallography (49).

The ^{115}In -NMR spectra of these anions have now been recorded, in each case using 0.1 M solutions in dichloromethane. The case of $\text{InBr}_2\text{Cl}_2^-$ well illustrates the findings; the spectrum (Figure 4) consists of five distinct lines. The extreme of these correspond to the resonance frequencies of InCl_4^- and InBr_4^- respectively. The intermediate lines are assigned to InCl_3Br^- , $\text{InCl}_2\text{Br}_2^-$ and InBr_3Cl^- . The same resonances were obtained from solutions prepared from either InBr_3Cl^- or InCl_3Br^- , although the relative intensities differed significantly in each of these three cases. Repetition of such experiments with other anions led to the results shown in Table 8. Results are not available for solutions of $\text{InBr}_2\text{I}_2^-$ or $\text{InCl}_2\text{I}_2^-$, but the ^{115}In frequencies for these anions could be deduced from the spectra of other salts.

It has also been shown experimentally that the multiline spectrum of any given $\text{InX}_n\text{Y}_{4-n}^-$ salt can be

Figure 4. Some typical ^{115}In -NMR spectra. Salts 0.1 M
in dichloromethane.

FIGURE 4

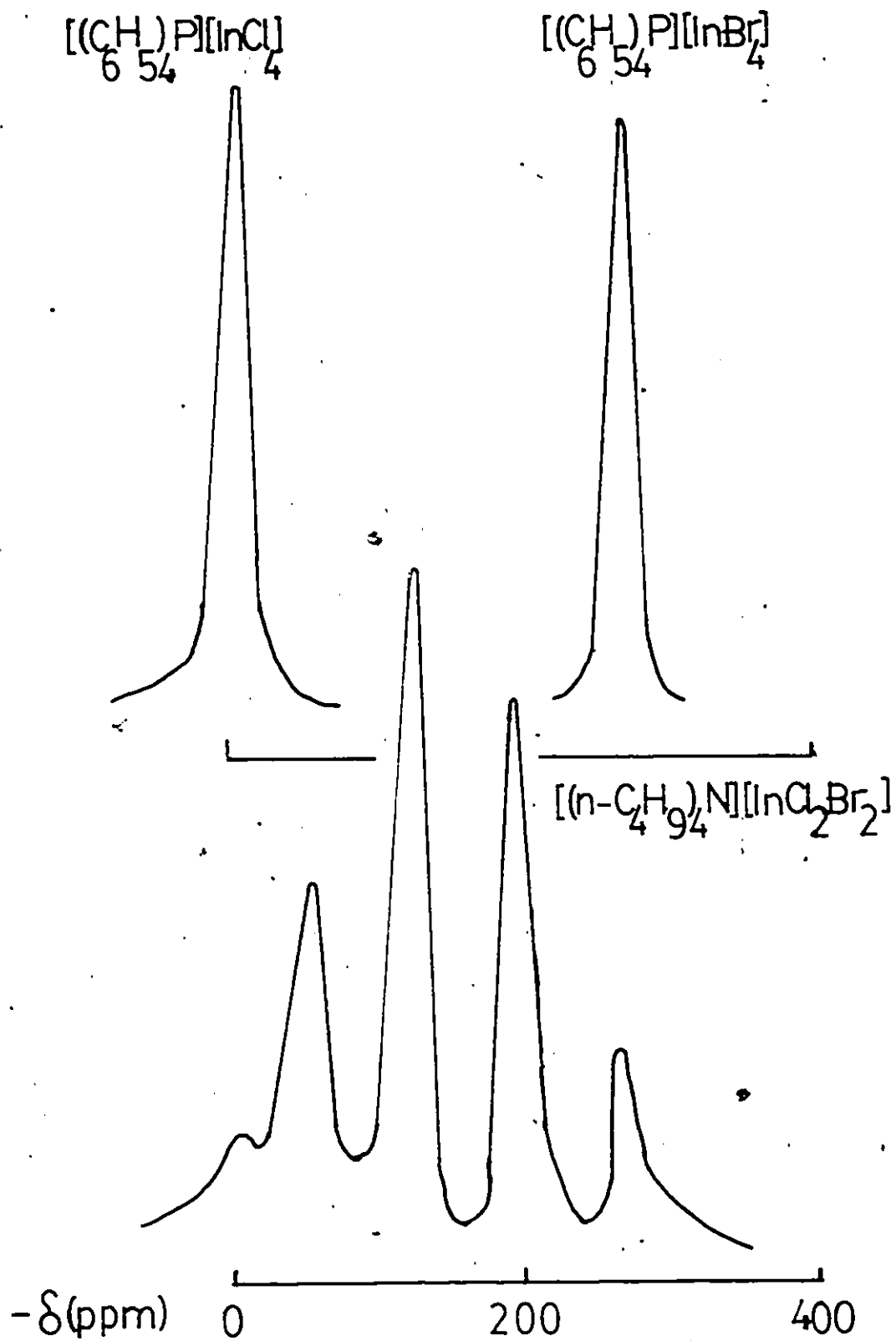


Table 8. Experimental ^{115}In resonances (in ppm) for $\text{InX}_n\text{Y}_{4-n}^-$ anions ($X \neq Y = \text{Cl}$, Br, I) in CH_2Cl_2 solution (a)

Parent Anion	Assignment (b)									
	InCl_4^-	InCl_3Br^-	$\text{InCl}_2\text{Br}_2^-$	InClBr_3^-	InBr_4^-	InBr_3I^-	$\text{InBr}_2\text{I}_2^-$	InBrI_3^-	InI_4^-	InClI_3^-
InCl_4^-	0									
InCl_3Br^-	0 (3.5)	-54 (3.5)	-120 (2)	-191 (1)	-269 (tr)					
$\text{InCl}_2\text{Br}_2^-$	-3 (tr)	-50 (2)	-114 (3)	-183 (3)	-258 (2)					
InClBr_3^-	0 (tr)	-54 (1)	-120 (2)	-191 (3.5)	-269 (3.5)					
InBr_4^-					-270					
InBr_3I^-					-258 (6)	-434 (3)	-626 (1)	-825 (tr)		
InBrI_3^-							-614 (2)	-810 (4)	-1010 (4)	
InI_4^-									-1010	
InClI_3^-									-1013 (4)	-711 (4)
InCl_3I^-									-706 (1)	-431 (3)
										-191 (6)

(a) Solutions prepared by dissolving tetra-*n*-butylammonium salt of parent anion in CH_2Cl_2 (0.1 mol L^{-1})

(b) Figures in parentheses are approx. relative intensities normalized to a total of 10; tr = detected, in small quantity.

reproduced by mixing solutions in the ratio $n \text{InX}_4^- / (4 - n) \text{InY}_4^-$, and that in the ultimate case, mixing equal volumes of 0.1 M solutions of InI_4^- , InBr_4^- and InCl_4^- results in a twelve-line spectrum. The analysis of all these results leads to Table 9. Three pairs of lines clearly overlap in the twelve line case, but only for $\text{InCl}_2\text{BrI}^-$ is there an absence of information from other experiments.

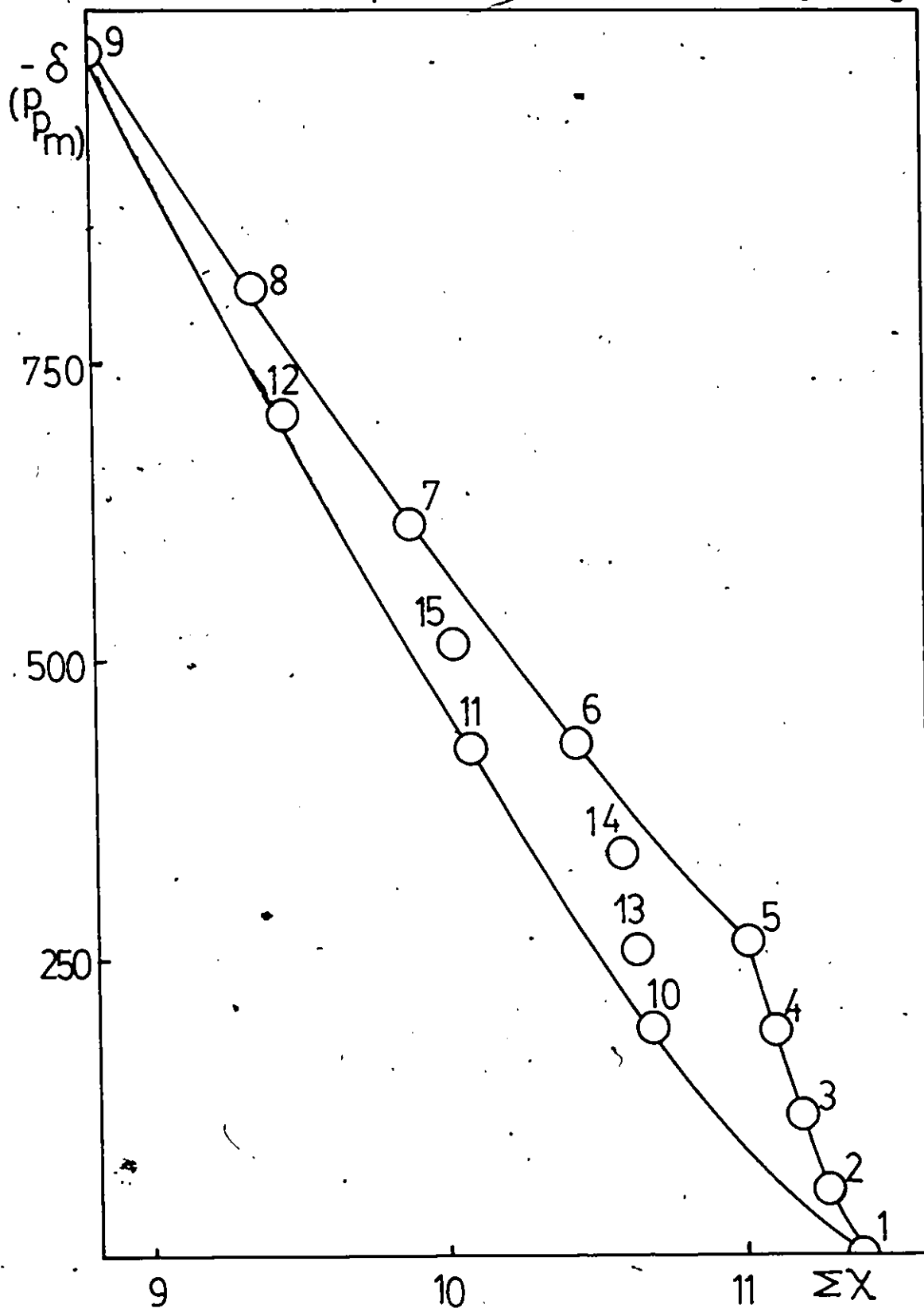
These results are similar to those reported for mixed $\text{AlX}_4^- / \text{AlY}_4^-$ (X as before) by Kidd and Truax (57) using ^{27}Al -NMR. The line widths of the C_{3v} and C_{2v} species are significantly greater than those of the tetrahedral anions, an effect which they ascribe to the lower molecular symmetry of the former. The same effect is evident in the present study. Redistribution reactions in the isoelectronic tin(IV) halides have also been studied by NMR methods (58), and the time for establishment of the equilibrium involving the series $\text{SnX}_4 - \text{SnX}_n\text{Y}_{4-n} - \text{SnY}_4$ ($X \neq Y = \text{Cl, Br, I}$) is estimated at between 10^{-3} and 10 sec. Almost identical values apply in the indium case; the maximum separation between adjacent lines defines the lower limit, and the establishment of the separate line spectrum within the minimum time of thirty seconds needed for mixing the solutions and collecting the spectrum fixes the upper limit. Results on similar gallium(III) systems have been reported quite recently; the rate at which equilibrium is reached in this case is slower by at least one order of magnitude,

with respect to the indium(III) and tin(IV) systems, and mechanistic speculations have been advanced on this basis (59).

Since the ^{115}In resonance frequency reflects the electron density at the nucleus, which is itself at the centre of the molecule, one might expect some simple dependence on ligand electronegativity. The results in Figure 5 show that such a relationship indeed holds, with the results falling in a series of three curves, one for each InX_4^- - InY_4^- series, using the Allred - Rochow values for χ . It has been suggested previously (41, 56) that both x-ray photoelectron spectra and vibrational stretching force constants for anionic indium(III) complexes demonstrate the strongly ionic nature of the In - X bond, and the data in Figure 5 generally confirm such model. The curves are non-linear, and markedly so for the chloride-iodide complexes, so that in any given series an $\text{InX}_n\text{Y}_{4-n}^-$ complex has a lower chemical shift than would be estimated by interpolation from the appropriate $\text{InX}_4^-/\text{InY}_4^-$ pair results, assuming a linear relationship between δ and $\Sigma\chi$. The results for the InX_2YZ^- anions show similar general trends, and the set InClBr_3^- - $\text{InClBr}_2\text{I}^-$ - InClBrI_2^- - InClI_3^- lie on a smooth curve. All in all, it is obvious that factors over and above ligand electronegativity are involved in determining δ , demonstrating that the ionic model is not a completely accurate description of the bonding. As expected, the effects of a significant covalent contribution show up most clearly in anions containing

Figure 5. ^{115}In chemical shift as a function of total ligand electronegativity for the series $\text{InX}_n\text{Y}_{4-n}^-$ and InX_2YZ^- . Key numbers refer to entries in Table 9.

FIGURE 5



In - I bonds:

The NMR results cast an interesting light on the earlier preparative and spectroscopic work* (Chapter 1). It seems that in solution, the behaviour of a mixture of InX_4^- - InY_4^- ions is identical to that of the corresponding $\text{InX}_n\text{Y}_{4-n}$ anion, so that the elaborate preparative route to the synthesis of the series of the latter species was probably unnecessary in such cases. In addition, it has been experimentally shown that a sample of $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{InCl}_3\text{Br}]$, characterized by x-ray diffraction studies (49), as well as vibrational spectroscopy, dissolves in ethanol to give a five-line ^{115}In -NMR spectrum, which is not significantly changed by raising the temperature (up to 70°C). On crystallization, the InCl_3Br^- species is again obtained and the residual liquid still shows a five-line spectrum. Thus the present results, and those of Chapter 1, are experimentally compatible. The origin of the impurities present in the solid samples subjected to vibrational studies, mentioned so often throughout Chapter 1, can then be explained by the set of simultaneous equilibria

$$\text{InX}_4^- \xrightleftharpoons{\text{InY}_4^-} \text{InX}_3\text{Y}^- \rightleftharpoons \text{InX}_2\text{Y}_2^- \rightleftharpoons \text{InXY}_3^- \xrightleftharpoons{\text{InX}_4^-} \text{InY}_4^-$$

where the composition of the species isolated from the solid phase is determined firstly by the stoichiometry of the parent material, and to a lesser extent by solubility factors.

2.8 MISCELLANEOUS ORGANOINDIUM(III) COMPOUNDS.

In view of the results obtained for the mixed haloanions of C_{3v} and C_{2v} symmetry, a series of experiments were carried out with the aim of determining the ^{115}In -NMR spectra of the organoindate(III) anions MeInX_3^- and $\text{Me}_2\text{InX}_2^-$ ($X = \text{Cl}, \text{Br}, \text{I}$).

No resonances could be detected in any of the cases above. This lack of features must then mean that perturbation of the spherical distribution of electronic charge about the indium nucleus in species as (say) InX_4^- is stronger when X is replaced by a Me substituent, and less so when the substituent is another halogen Y.

The same symmetry argument needs to be invoked in connection with the series Me_2InX (X as before). These compounds have been formulated as the neutral halogen dibridged dimers $\text{Me}_2\text{InX}_2\text{InMe}_2$ in the solid state (60), and accordingly no ^{115}In resonances were detected for solutions of these materials in acetonitrile, acetone or chloroform. A similar situation pertains to the series Ph_2InX ($X = \text{Cl}, \text{I}$).

2.9 CONCLUSIONS.

The use of ^{115}In -NMR spectroscopy for the purpose of structural characterization is, at the present time, restricted to species in which the electron distribution about the metal nucleus is spherical, or nearly so. This can, in some cases, be considered an advantage, since tetrahedral species are almost unequivocally characterized

in solution (cf. Chapter 3 for an illustration of this statement).

The solution properties of the anionic halides of indium have been confirmed in a number of points, and additional useful information has been obtained in the specific cases of the $\text{InX}_4^-/\text{X}^-$ and the mixed halide systems.

CHAPTER 3

COMPLEXES OF INDIUM(I) AND INDIUM(III) WITH SOME MACROCYCLIC LIGANDS

3.1 INTRODUCTION.

One interesting feature in the chemistry of the Main Group IIIa is the differing degree of occurrence of low valent derivatives in different members of the Group.

While for the lighter elements boron, aluminum and gallium the coordination chemistry of the oxidation states I and II is for all practical purposes unknown, the heavier element in the Group, thallium, displays a rather rich chemistry in this respect.

Indium is intermediate between gallium and thallium in this context. The binary monovalent derivatives InX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been known for some time, but their use in synthetic work is limited by their lack of solubility in most common solvents. Despite this disadvantage, anionic materials of the type $[\text{Me}_2\text{Bipy}]^{2+} [\text{InX}_3]^{2-}$ (X as before) have been obtained from the reaction of the monohalides and the corresponding bipyridinium halides. The vibrational spectra of these species were assigned on the basis of a C_{3v} symmetry for the anion (61).

Other reports have claimed the preparation of materials of composition InL_4X ($\text{L} = \text{aniline}, \text{morpholine};$ X as before) from the reaction of indium(I) halides and the

free ligands (62), but no structural details have been given. Equally vague descriptions have been offered for the mono- and bis- adducts of ammonia and indium(I) halides (63).

Cyclopentadienylindium(I) has been found to be a useful starting material for the preparation of neutral and anionic indium(I) compounds. Materials of composition InB have been obtained from the organoindium(I) compound and the protonated molecules HB (quinoline, substituted pentane-2, 4-diones) (30). Chapter 1 also made reference to the anions InX_2^- ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), for which a monomeric structure of C_{2v} symmetry has been proposed (19).

The presence of the indium(I) cation has been presumed in the materials InX_2 and In_2X_3 , respectively formulated as the ionic dimers $\text{In}[\text{InX}_4]$ (61) and $\text{In}_2[\text{In}_2\text{X}_6]$ (64) ($\text{X} = \text{Br}, \text{I}$, but not Cl), although it should be clear that these formulations do not add to the knowledge of monovalent indium compounds.

This Chapter describes a series of experiments, carried out in an attempt to stabilize the indium(I) species by complexation with large, chelating ligands. The principle of bulky donor molecules stabilizing unusual oxidation states has met with considerable success in transition metal, as well as main group chemistry (65). The only previous work related to indium chemistry in this area refers to the reaction of porphyrins with trivalent indium (1, 66), although there has been a detailed preparative study of the complexes formed

by thallium(I) salts and a number of crown ethers (67).

This work has been concerned with the reactions of the polyether 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6 = crown), the nitrogen donor 1,4,8,11-tetraazacyclotetradecane (cyclam) and indium I, II and III halides, and certain organoindium halides. The structures of the products, which include the first unambiguous cationic indium(I) species, were elucidated by vibrational spectroscopy.

3.2 EXPERIMENTAL.

InAlCl_4 , first described by Clark, Griswold and Kleinberg (20), was prepared by refluxing equimolar quantities (typically 10 mMol) of InCl and AlCl_3 in 50 mL mixed xylenes. After 10 hrs. the insoluble material was removed by filtration, the filtrate evaporated down to 10 mL, and 30 mL petroleum ether added; the resultant solid was collected, washed with petroleum ether and dried.

Cyclam was prepared by the reaction of 1,3-dibromopropane with ethylenediamine (68), dibenzo-18-crown-6 (Alfa) was used as supplied.

Preparative - Equimolar amounts (typically 5 mMol, all species calculated as monomers) of the appropriate indium compound and the macrocyclic ligand were refluxed in 50 mL of benzene. In all cases, signs of reaction were evident after the first two hours, but experience showed that the

Table 10. Analytical results for indium complexes with macrocyclic ligands

	Found(%)		Required(%)	
	In	Halogen	In	Halogen
$\text{In}_2\text{Cl}_4(\text{crown})$	31.9	19.5	31.5	19.4
$\text{In}_2\text{Br}_4(\text{crown})$	24.7	35.0	25.3	35.2
$\text{In}_2\text{I}_4(\text{crown})$	20.3	45.9	20.9	46.3
$\text{InAlCl}_4(\text{crown})$	18.0	22.3	17.9	22.0
$\text{In}_2\text{Cl}_6(\text{crown})$ (a)	28.8	27.5	28.6	26.6
$\text{In}_2\text{Br}_6(\text{crown})$	21.0	44.3	21.5	44.9
$\text{In}_2\text{I}_6(\text{crown})$	16.6	55.8	17.0	56.4
$\text{In}_2\text{Me}_2\text{I}_4(\text{crown})$	20.9	44.5	20.4	45.1
$\text{In}_2\text{Cl}_4(\text{cyclam})$	40.7	25.0	40.2	24.8
$\text{In}_2\text{Br}_4(\text{cyclam})$	31.5	43.0	30.7	42.7
$\text{In}_2\text{I}_4(\text{cyclam})$	24.3	54.7	24.5	54.2
$\text{InAlCl}_4(\text{cyclam})$	22.8	28.9	23.8	29.3
$\text{In}_2\text{Cl}_6(\text{cyclam})$ (b)	35.7	33.0	35.8	33.2
$\text{In}_2\text{Br}_6(\text{cyclam})$	52.8	25.2	52.7	25.3
$\text{In}_2\text{I}_6(\text{cyclam})$	19.4	63.9	19.3	63.7

(a) Found C 29.3, H 3.2; required C 29.9, H 3.0

(b) Found C 17.9, H 3.9, N 8.5; required C 18.7, H 3.7, N 8.7

materials isolated at this point were not analytically acceptable, so that as a general rule reflux was continued for at least another 10 hrs., and in some cases for 24 hrs., after which the resulting suspension was filtered hot and the collected solids washed with 50 - 100 mL of hot benzene. Approximately one half of the original quantity of ligand was recovered from the mother and wash liquors. The solid products were dried overnight in vacuo at 105°C. Analytical results are given in Table 10; here and elsewhere, the cyclic ligands are abbreviated as 'crown' and 'cyclam' respectively. The products are off-white powders except for In_2I_4 (cyclam) which is red, and In_2Br_4 (cyclam) which is orange.

All the compounds are insoluble in aromatic and aliphatic hydrocarbons. Attempts to recrystallize the products from basic solvents (acetone, acetonitrile) or chloroform lead to decomposition, with release of the free ligand (see NMR results below), and the deposition of solids which in the case of the In_2X_4 derivatives were identified as indium(I) halides.

3.3 LIGAND COMPLEXATION.

Before moving to a discussion of the structural assignments, it seems appropriate to review the evidence for complexing by the crown and cyclam ligands in the products isolated.

Three bands in the infrared spectrum of the free

crown ether can be associated with C-O stretching, namely those at 1133, 1262 and 1236 cm^{-1} . In a typical system, such as In_2I_6 (crown), the 1133 band is split into three components at 1075, 1108 and 1138 cm^{-1} , while the remaining pair moves to 1216 and 1267 cm^{-1} . Similar features are observed in the other crown ether derivatives. Unfortunately, the complexity of the spectrum prevents a detailed analysis of these features. The ^1H -NMR spectrum (acetone- d_6 solution) confirms the alteration of the electronic density around the oxygen atoms on complexation. The aromatic signal at 6.90 ppm from external TMS in the free ligand shifts to 7.10 ppm upon complexation, while the A_2B_2 multiplet centered at 3.95 ppm appears at 4.25 ppm in the complexes. The pattern of the multiplet does not change as a result of complex formation, suggesting that at least in this solvent either the mode of donation is symmetric, or that the sites of coordination are exchanging quickly on the NMR time scale. The spectrum of a freshly prepared solution of a crown ether-indium complex changed within 5 - 10 minutes, and the resonance pattern of the free ligand was eventually the only observable feature.

In the cyclam systems the broad ir band at 1140 cm^{-1} , assigned to a general "C-N stretching" mode, does not change appreciably upon coordination. Clearer evidence is obtained from the (N-H) region of the spectrum, where bands at 3270 and 3200 cm^{-1} in free cyclam are shifted to 3320 and 3240 cm^{-1} respectively, with a

significant increase in intensity. The proton NMR spectrum of cyclam in CDCl_3 includes, inter alia, a broad singlet (2.30 ppm from external TMS) which disappears in D_2O solution and is therefore assigned to the N-H proton. This resonance sharpens and moves to 2.50 ppm on complex formation; the other resonances are unchanged.

The spectral changes summarised above were detected in all the compounds prepared, and thus confirm the existence of complexes of these ligands. The subsequent discussion focusses on the use of In-X vibrations in the further characterisation of these complexes.

3.4 INDIUM MONOHALIDES.

Repeated attempts at reacting indium(I) halides with crown or cyclam gave negative results. This is surprising, since complexes of thallium(I) with various crown ethers, including dibenzo-18-crown-6, have been reported (67), and considering the successful isolation of cationic indium(I) derivatives (see below); the low solubility of indium(I) halides, which has been remarked upon previously, may be at the root of this unreactivity.

3.5 INDIUM DIHALIDES.

The reactions of InX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with both crown and cyclam lead to compounds of stoichiometry $\text{In}_2\text{X}_4\text{L}$. The species most easily identified from the vibrational spectra of these products are the InX_4^- anions

(see Table 11). The assignments are readily made on the basis of early work in solid state (21) and solution (38-40). The ν_1 modes are detected in the Raman spectra, which also demonstrate the absence of molecules with an In-In bond (cf. Chapter 4). The splitting of ν_3 , and the detection of ν_1 as a weak feature of the infrared spectra, are ascribed to a lowering of the T_d symmetry in the solid state, and interactions between InX_4^- and the cation may be the cause of this distortion.

The presence of InX_4^- implies the existence of $[\text{In}(\text{crown})]^+$ and $[\text{In}(\text{cyclam})]^+$ cations, and again the vibrational spectra support this formulation. Indium-oxygen stretching vibrations have been observed in a number of relevant compounds. The band at 444 cm^{-1} in the Raman spectrum of $\text{In}(\text{acac})_3$ has been assigned (69) as $\nu(\text{In}-\text{O})$, and a similar assignment has been made for an ir feature at 454 cm^{-1} in the adducts $\text{InX}_3 \cdot 2\text{Et}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$) (70, 71), for which group theory predicts one ir active mode (A_2'') in D_{3h} symmetry. Similarly, Carty and Patel (72) have identified strong ir bands between 400 and 460 cm^{-1} in the spectra of a series of In - DMSO complexes as In - O stretching modes. Table 11 shows that each of the crown ether compounds absorbs in the 340 cm^{-1} region, and these vibrations are tentatively assigned as $\nu(\text{In}-\text{O})$, with reduction in frequency from the values just noted ascribed to the formation of In - O bonds involving the heavy cyclic ligand. This argument is supported by that given below for indium(III)

Table 1.1.

The vibrational spectrum of $\text{In}_2\text{X}_4\text{L}$ and $\text{InAlCl}_4(\text{crown})$ (cm^{-1})
 (X = Cl, Br, I; L = crown, cyclam)

	Cation		InX_4		Unassigned	
	$\nu(\text{In-L})$ ir	$\nu_3(\text{F}_2)$ ir	$\nu_1(\text{A}_1)$ ir(a)	$\nu_4(\text{F}_2)$ ir	ir	
$\text{In}_2\text{Cl}_4(\text{crown})$	351m(b)	297s 312vs 342m	322m	110m 120w	169w	
$\text{In}_2\text{Br}_4(\text{crown})$	340w	205s 215vs 220s	188w 230vw	194s masked		
$\text{In}_2\text{I}_4(\text{crown})$	336m	184s 193s	188w 135w	139s 60m(c)	75m	
$\text{InAlCl}_4(\text{crown})$	334w	486vs 494s	357s(d)	135(d,e)		
$\text{In}_2\text{Br}_4(\text{cyclam})$	403w	242m 230m	190m			
$\text{In}_2\text{I}_4(\text{cyclam})$		176vs 188s	186w 139s	56w	210w	

(a) Breakdown of selection rules by symmetry lower than T_d in the solid

(b) Weak Raman feature at 359 cm^{-1}

(c) Medium intensity Raman line at 56 cm^{-1}

(d) Vibrations of AlCl_4^-

(e) Raman

derivatives; the spectra of the latter show that some additional weak features in the spectra of the $\text{In}_2\text{X}_4(\text{crown})$ arise from contamination by the appropriate $\text{In}_2\text{X}_6(\text{crown})$, produced by disproportionation of the low valent moiety.

For the cyclam systems, the most relevant comparison is with the dimer $(\text{Me}_2\text{InNMe}_2)_2$, for which a series of bands in the range $420 - 490 \text{ cm}^{-1}$ are assigned to In - N stretching modes in the In_2N_2 ring (73). Tables 11 and 12 show that the cyclam derivatives have weak absorptions at 397 to 400 cm^{-1} , which by the argument given above for the crown complexes can reasonably be identified as In-N stretching modes.

Since the complexes decompose in solution, it proved impossible to measure the molar conductivity, or to prepare salts of InL with large anions by way of structural confirmation. However, reaction of InAlCl_4 and the crown ether yielded a material similar to the ones described above, containing the indium-free anion AlCl_4^- , whose vibrational spectrum is clearly observed (see Table 11 and reference (74)). The corresponding cyclam analogue could not be isolated, since decomposition with evolution of HCl was evident during the reaction; the disappearance of the N - H stretching features and other skeletal changes in the cyclam ligand were also observed in the ir spectrum of this material.

The spectral results then are consistent with the formulation of these compounds as salts of $[\text{In}(\text{crown})]^+$

and $[\text{In}(\text{cyclam})]^+$ cations. One exception to this conclusion is the product of the reaction between InCl_2 and cyclam; the analytical results for this compound do not fit the $\text{In}_2\text{Cl}_4(\text{cyclam})$ formulation particularly well, and the gray appearance of the product is similar to that associated with the presence of indium metal, implying disproportionation of indium(I). The identification of $[\text{In}(\text{crown})]^+$ is supported by the work of Herber and Smelkinson (75), who isolated $\text{Sn}_2\text{Cl}_4(\text{crown})$, formulated as $[\text{Sn}(\text{crown})]^{2+} [\text{SnCl}_4]^{2-}$, on the basis of Mossbauer spectroscopy.

3.6 INDIUM TRIHALIDES.

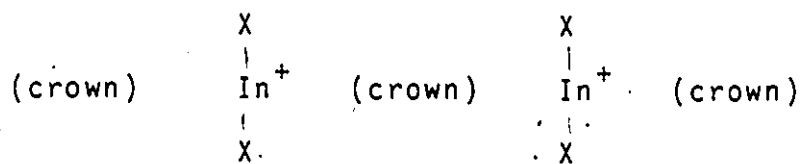
The products of the reaction between indium(III) halides and crown or cyclam are a group of $\text{In}_2\text{X}_6\text{L}$ species. The presence of the InX_4^- anion is again evident from the vibrational spectra (Table 12), leading to a possible formulation $[\text{InX}_2\text{L}]^+ [\text{InX}_4]^-$. A number of similar structures have been suggested for indium(III) halide adducts (1). The $\nu_1(\text{A}_2)$, $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ modes of the InX_4^- anions were observed in each case; splitting of ν_3 occurs in the ir, but is less pronounced than in the $\text{In}_2\text{X}_4\text{L}$ series. There is a sharp distinction between the crown ether and cyclam complexes, in that the spectra imply a completely different structure for the latter (see below).

The structure of the cationic moiety is more difficult, but the vibrational spectra give some guidance

as to a possible formulation. We first note that bands observed at approximately 330 cm^{-1} in the crown complexes are tentatively assigned as $\nu(\text{In} - \text{O})$, following the argument above for the indium(I) species, showing that there is little change in this frequency with oxidation state. The $\nu(\text{In} - \text{X})$ bands are more informative. Group theory predicts one $\text{In} - \text{X}$ stretching mode in the ir if the $\text{X} - \text{In} - \text{X}$ moiety is linear, with a non-coincident Raman mode, while two bands are expected in each effect for a bent InX_2 skeleton. The better fit to the spectral results is obtained with the second possibility. Raman modes at 150 and 206 cm^{-1} are observed for the I and Br/crown systems respectively, with weak coincident ir features. The spectra of $\text{In}_2\text{Cl}_6(\text{crown})$ are less easily assigned, since the relevant frequency range is overlapped by $\nu(\text{In} - \text{O})$ and by ν_3 of InCl_4^- , but a Raman band at 332 cm^{-1} is reasonably attributed to $\nu_{\text{sym}}(\text{In} - \text{Cl})$ of $[\text{InCl}_2(\text{crown})]^+$. The ir spectra show bands at 256 , 307 and 406 cm^{-1} for the I, Br and Cl species respectively, assigned to $\nu_{\text{asym}}(\text{In} - \text{X})$. The corresponding Raman emissions are weak, but quite detectable in the iodide case. It is noteworthy that the ir spectra also have bands attributable to bending modes of the InX_2 units in the cations (Table 12). The large frequency separation between the symmetric and antisymmetric stretchings, together with the weak intensity of the $\nu_{\text{sym}}(\text{In} - \text{X})$ bands in the ir, and of the $\nu_{\text{asym}}(\text{In} - \text{X})$ in the Raman, suggest that the InX_2 unit may be close to linear

in the solid state. The breakdown of the mutual exclusion rule for a linear MX_2 species may be the result of interactions between anion and cation in the solid state, in keeping with the splitting observed for ν_3 of the InX_4^- anion. Before discussing the structural implications of a linear InX_2 unit, it is worth noting the close similarity between the frequencies assigned above, and the corresponding values for the isoelectronic CdX_2 molecules. Raman studies (76) of CdX_2 in solution lead to identification of ν_1 for the linear, solvated species, while the ir spectra of CdX_2 molecules in the gas phase lead to values for $\nu_{\text{asym}}(\text{Cd} - \text{X})$ (77). The difference in phase raises some questions, but the comparison between these results and the present values is striking (see Table 13).

In the light of this evidence, it is believed that the existence of linear X-In-X^+ units is well established. There are then two structural formulations, either a mononuclear $[\text{InX}_2(\text{crown})]^+$ species with *trans* halide ligands, or a polymeric structure of the type



in which each indium is coordinated by one or more oxygen atoms from each of two crown ether molecules. Earlier work (78) on the coordination number of indium(III) suggests that a InO_4X_2 kernel is likely, requiring the donation from two pairs of oxygen atoms. The available evidence does not

Table 12. The vibrational spectra of $\text{In}_2\text{X}_6\text{L}$ (cm^{-1}) ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{L} = \text{crown}, \text{cyclam};$
all combinations)

		$\text{In}_2\text{Cl}_6(\text{crown})$	$\text{In}_2\text{Br}_6(\text{crown})$	$\text{In}_2\text{I}_6(\text{crown})$	$\text{In}_2\text{Cl}_6(\text{cyclam})$	$\text{In}_2\text{Br}_6(\text{cyclam})$	$\text{In}_2\text{I}_6(\text{cyclam})$
		(b)					
$\nu(\text{In-L})$	ir	masked	316m, 346w	340w	410w	404w	397m
$\nu(\text{In-X})_{\text{as}}$	{ir Ra}	406m 405w	307m	256w 260w			
Cation							
$\nu(\text{In-X})_{\text{s}}$	{ir Ra}	masked 332m	203vw 206m	148w 150s		206w 206w	
$\delta(\text{InX}_2)$	ir	190w	164vw				
$\nu_3(\text{F}_2)$	{ir Ra (c)}	334vs, 342sh masked	228s, 235s 230w	184vs, 194s 188w	336vs, 342s	{229sh, 236vs, 243sh}	{178s, 185s, 192s, 188m}
InX_4^-							
$\nu_1(\text{A}_1)$	{ir Ra}	320sh 322m	194w 196s	136w 138s	190m 194w	148m 139s	
$\nu_4(\text{F}_2)$	ir	114m	80w	58m (d)	122m	80w	
Unassigned							
	ir	90w			286m, 250w	90w	360w
	Ra					118w, 110w	

(a) Sample strongly fluorescent. Raman results not available. (b) Weak Raman feature at 320 cm^{-1}

(c) Breakdown of selection rules by symmetry lower than Td in the solid.

(d) Median intensity Raman counterpart at 57 cm^{-1} .

Table 13. Comparison of ir frequencies (cm^{-1}) for CdX_2 and InX_2^+

	CdX_2			InX_2^+		
	ν_{sym}	ν_{asym}	mean	ν_{sym}	ν_{asym}	mean
Cl	280	427	353	332	406	369
Br	186	315	250	206	307	257
I	144	265	205	150	256	203

allow a clear choice to be made between the two proposed structures at the present time.

The results in Table 12 for the $\text{InX}_3/\text{cyclam}$ systems do not lead to an analysis such as that given for the crown ether complexes. There are no In-X stretching modes other than those assignable to anionic indium(III) complexes, with the exception of a weak band at 206 cm^{-1} in the bromide case. The simplest explanation of these results is that the cyclam is a sufficiently strong ligand to displace halide completely from In^{3+} . The stoichiometry of the products then requires the solid state to be

$\text{In}(\text{cyclam})_2^{3+} + 3\text{InX}_4^-$, with indium probably six-coordinate in the cation (cf. reference (78)).

3.7 ORGANOINDIUM HALIDES.

In view of previous interest in the acceptor properties of organoindium(III) halides (14, 15) we have briefly investigated the interaction of CH_3InCl_2 and CH_3InI_2 with crown and cyclam. In the case of the latter ligand, it was not possible to identify the reaction products on the basis of the analytical results. The best characterised product has the stoichiometry $(\text{CH}_3)_2\text{In}_2\text{I}_4(\text{crown})$, and in view of the structure of the starting material (14), $[(\text{CH}_3)_2\text{In}][\text{InI}_4]$, and the work described above, the formulation $[(\text{CH}_3)_2\text{In}(\text{crown})][\text{InI}_4]$ appeared most probable. In fact, the infrared spectrum of this material below 500 cm^{-1} (and of the corresponding chloride analogue)

clearly reveals the presence of the $\text{CH}_3\text{InX}_3^-$ anion, whose electrochemical preparation was referred to in Chapter 1 (see Table 14 for details). At the same time, a strong band at 184 cm^{-1} indicates that InI_4^- anions are also present. The ^1H -NMR spectrum equally identifies $\text{CH}_3\text{InI}_3^-$, and indicates the presence of a second In-CH_3 species in the solution. Finally the presence of InX_4^- ($\text{X} = \text{Cl}, \text{I}$) in acetonitrile solution was confirmed by ^{115}In -NMR spectroscopy, with chemical shifts of -2 and -1003 ppm respectively from $(\text{C}_4\text{H}_9)_4\text{NInCl}_4$; these values are identical within experimental error to those found for authentic samples of InCl_4^- and InI_4^- (see Chapter 2 for details). From this evidence, it appears that we are dealing with a mixture of $[(\text{CH}_3)_2\text{In}(\text{crown})][\text{InI}_4]$ and $[\text{CH}_3\text{InI}(\text{crown})][\text{CH}_3\text{InI}_3]$ in both solid and solution phases. Attempts to separate the components were unsuccessful, and redistribution of ligands appears to occur rapidly in solution.

3.8 CONCLUSIONS.

The reaction between indium dihalides and the macrocyclic ligands crown and cyclam affords a route to the preparation of cationic complexes of indium(I). The size of the ligands and their ability to block simultaneously all coordination positions in the low valent metal cation perhaps prevent extensive decomposition via disproportionation.

Vibrational spectroscopy establishes with certainty the existence of $\text{InX}_2(\text{crown})^+$ cations, with linear InX_2^+

Table 14. Some organoindium derivatives of dibenzo-18-crown-6-ether

	$^1\text{H-NMR}$ (a)	ir (cm^{-1})
$\text{In}_2\text{Me}_2\text{I}_4(\text{crown})$	0.67(s,3), 0.60(s,3)	501m, 197s, 184s, 166s, 150m
$\text{Bu}_4\text{N MeInI}_3$ (b)	0.67(s,3)	496s, 165vs, 152m
$\text{MeInCl}_2/\text{crown}$ (c)	0.20(s), 0.07(g) (d)	512m, 329m, 294vs, b, 208m, 120s
$\text{Et}_4\text{N MeInCl}_3$	0.07(s)	522s 290vs, b, 206m, 120s

(a) All resonances in acetone- d_6 , in ppm downfield from external TMS.

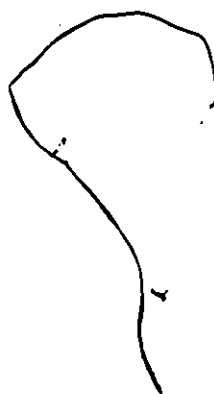
(b) Material made from methylindium dihalide and the ammonium salt.

(c) Material not characterised by analysis.

(d) Intensity of the signals varies after approx. 5 min.

5

units, in those materials formulated as $\text{In}_2\text{X}_6(\text{crown})$.



CHAPTER 4

SOME NEUTRAL ADDUCTS OF In_2Br_4 and In_2I_4

4.1 INTRODUCTION.

The previous chapter commented on the lack of information pertaining to the chemistry of the low valent derivatives in elements of the Main Group III. For indium(I), neutral (30), cationic ((79) see also Chapter 3) and anionic (19, 60, 80, 81) complexes are now known.

While occurrence of the monovalent state increases down the Group from gallium to thallium, the reverse seems to be the case for the divalent derivatives.

There is no evidence for the existence of divalent thallium compounds (82) save for the species $\text{K}_2\text{Tl}_2\text{Me}_6$, referred to in Chapter 5.

For gallium, the anions $\text{Ga}_2\text{X}_6^{2-}$ have been isolated as tetraalkylammonium salts for all three halides Cl, Br and I (83). The crystal structures of $(\text{Me}_4\text{N})_2\text{Ga}_2\text{Cl}_6$ (23), $[(i\text{-Pr})_4\text{N}]_2\text{Ga}_2\text{Br}_6$ (84) and $(\text{Ph}_3\text{PH})_2\text{Ga}_2\text{X}_6$ ($\text{X} = \text{Cl}, \text{I}$) (85) have been published. The existence of the anion $\text{Ga}_2\text{I}_6^{2-}$ is postulated in Ga_2I_3 , formulated as $\text{Ga}_2[\text{Ga}_2\text{I}_6]$ on the basis of vibrational spectroscopy (86, 87). In all these compounds the anions feature two GaX_3^- units joined by metal-metal bonds.

Neutral adducts of gallium(II) are also known. Partial replacement of the dihalide ions in $\text{Ga}_2\text{X}_6^{2-}$ by

diethyl ether leads to compounds formulated as $(Et_2O)_X Ga-GaX_2(Et_2O)$ (82). More recently, Worrall *et al.* have published details of the preparation of $(Diox)Cl_2 Ga-GaCl_2(Diox)$. X-ray diffraction studies on this material established it as a metal-metal bonded species, in which the $Ga_2Cl_4O_2$ kernel displays C_{2h} symmetry (88).

Related advances on divalent indium derivatives parallel those described above for gallium. The subhalides In_2Cl_3 (melt) (89) and In_2Br_3 (90) are formulated as the ionic species $In_2[In_2X_6]$, based on their vibrational spectra. The hexahalogenodiindate(II) anions have also been prepared as tetra-n-butylammonium salts and their structures have been assigned as D_{3h} , ethane-like, staggered conformations, on the basis of vibrational data (13).

This Chapter describes the preparation of a small number of neutral adducts of the indium dihalides. The only previous example in which the stoichiometry might point to a neutral adduct formulation is $In_2I_4 \cdot 2Bipy \cdot 4NH_2Et$. Unfortunately, no structural studies have followed the original report on its preparation (91). Substantial advances are expected in the field of neutral adducts of indium(II) in the near future (92).

On the basis of the vibrational spectra, the adducts reported here are believed to contain indium-indium bonds. These are similar to the gallium analogues reported by Worrall *et al.* (88), although it appears that the

symmetry and coordination numbers at the metal may not be the same for some of the compounds discussed here.

4.2 EXPERIMENTAL.

Preparative. The same general method was used in each case, with isolation procedures which varied according to the particular system. Approximately 2-3 mmol of the dihalide (calculated as the dimer) was placed in a Schlenk flask and 30-40 mL of benzene syringed in through a rubber septum. The resultant suspension was frozen in liquid nitrogen, and a four-fold excess of monodentate, or two-fold excess of bidentate, ligand syringed in; solid ligands were dissolved in the minimum amount (5 - 10 mL) of benzene for this purpose. The liquid nitrogen cooling bath was removed and the system stirred as soon as the melting of the solvent allowed. Magnetic stirring was continued for 20 min. after the solvent had completely melted.

Isolation Procedures. InBr₂/TMED: The white suspension was filtered and the solid collected and dried. Analysis established the composition InBr₂(TMED) for this material. The mother liquors were allowed to stand over a period of 72 hrs., when large crystals (1.5 x 0.5 x 0.5 cm) were obtained, with further smaller (1 x 1 x 2 mm) crystals being obtained from the residual liquid after 24 hrs. These crystals had the composition In₂Br₄(TMED)₂C₆H₆.

InI₂/TMED: A red colour, believed to indicate

Table 15. Analytical results for some neutral adducts of the indium dihalides

	Found(%)		Required(%)	
	Indium	Halide	Indium	Halide
$\text{In}_2\text{Br}_4(\text{Et}_3\text{P})_2$	29.0	41.0	29.3	40.7
$\text{In}_2\text{Br}_4(\text{TMED})_2$	32.7(a)	39.2(a)	29.4	40.9
$\text{In}_2\text{Br}_4(\text{TMED})_2\text{C}_6\text{H}_6$	26.8	37.3	26.7	37.2
$\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$	24.1	52.1	23.6	52.2
$\text{In}_2\text{I}_4(\text{TMED})_2$	23.6	52.9	23.7	52.4
$\text{In}_2\text{I}_4(\text{TMED})_2\text{C}_6\text{H}_6$	22.2	48.4	21.9	48.5

(a) See text for discussion of these analyses

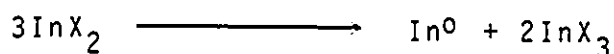
the presence of InI, was still apparent after stirring at room temperature for 2.5 hrs., and the mixture was therefore refluxed for two hours. The yellow solid which separated on cooling was collected and dried, and found to have the composition $\text{InI}_2(\text{TMED})$. The filtrate was concentrated to 20 mL and a viscous brown liquid settled out on standing. This oil was separated and treated with 10 mL of light ligroin (40 - 60° bp) to yield a sticky yellow solid which was exhaustively pumped at room temperature. Analysis showed the composition of this material to be $\text{In}_2\text{I}_4(\text{TMED})_2\text{C}_6\text{H}_6$. The same material was obtained by a reaction of equimolar amounts of indium(I) iodide and indium triiodide in the presence of a two-fold excess of TMED, in refluxing benzene.

InBr₂/Et₃P: When these two substances reacted in toluene at -40°C, a deep red solution initially formed but this rapidly changed colour, becoming yellow at about -20°C, and at room temperature appreciable decomposition to the metal was noted. Addition of cold light ligroin to the solution at -20°C produced a white precipitate which was collected and dried; analysis gave the empirical formula $\text{InBr}_2 \cdot \text{Et}_3\text{P}$. The instability of this material prevented further investigation, and in particular the infrared and Raman spectra presented no identifiable features.

InI₂/Et₃P: The green reaction mixture was concentrated to 20 mL by evaporation; after 2 - 3 hrs. the orange crystalline material which was deposited was

collected and dried. Further material was obtained by addition of light ligroin to the solution. Analysis showed this solid material to be $\text{InI}_2 \cdot \text{Et}_3\text{P}$.

Other Reactions. Reactions between benzene solutions of InBr_2 and the ligands Et_3N , pyridine, 2,2'-bipyridine and dimethylsulphoxide all gave indium metal in yields of 90% or larger, according to the disproportionation reaction



In the case of $\text{InBr}_2/\text{Et}_3\text{P}$, a substance of stoichiometry $\text{InBr}_3 \cdot 2\text{Et}_3\text{P}$ was recovered from the mother liquor, while $\text{InBr}_2 + \text{Ph}_3\text{P}$ yielded 100% InBr according to $\text{In}_2\text{Br}_4 \longrightarrow \text{InBr} + \text{InBr}_3$. Similar behaviour was observed with InI_2 and Et_3N , pyridine, 2,2'-bipyridine, Ph_3P , and bis(diphenylphosphino)ethane.

All attempts to make chloro-derivatives by the above methods from InCl_2 and a number of neutral donors resulted in disproportionation to indium metal.

4.3 GENERAL.

The presence of coordinated ligands is apparent from the analytical results and from infrared spectroscopy. The ir spectrum of neat TMED has bands *inter alia* at 1040 and 1275 cm^{-1} , which are shifted to 1025 and 1295 cm^{-1} in the complexes, suggesting that they are related to the vibrations of the donor atom (93). Similarly, bands at 1230 and 975 cm^{-1} in the spectrum of Et_3P (94) shift to

1265 and 995 cm^{-1} in the complexes. ^1H -NMR spectra of the products in deuteroacetonitrile also confirmed the presence of the ligands without adding to a knowledge of the structures of the complexes. The magnetic susceptibilities of the solid materials (0.01 - 0.05 B.M. at 25°C) established them as diamagnetic. Rapid decomposition in suitable solvents prevented the measurement of molar conductivities.

Sharp aromatic resonances (7.20 ppm downfield from TMS) confirmed the presence of benzene in those products formulated as $\text{In}_2\text{X}_4(\text{TMED})_2\text{C}_6\text{H}_6$. Neither NMR nor vibrational spectroscopy throws any light on the mode of interaction of benzene in the solid phase of such compounds, and only minor changes in other frequencies were noted on comparing analogous solvated and non-solvated compounds. This may indicate that the benzene is merely trapped in the crystal lattice with no strong interactions towards the metal centre, and in keeping with this, the crystalline materials slowly lose benzene and disintegrate on standing in an atmosphere of dry nitrogen, which frustrated attempts at x-ray structural analysis.

4.4 VIBRATIONAL SPECTROSCOPY.

In view of the above results, it is concluded that the most obvious structural analogues of these compounds are the $\text{Ga}_2\text{Cl}_4\text{L}_2$ compounds reported by Worrall *et al.* (88), and shown to involve Ga-Ga bonding. The presence of In-In bonds in the corresponding indium(II)

anionic complexes also provides further indication of a metal-metal bonded structure, and in the absence of x-ray crystallographic data (see above) the formulation of the present compounds as In-In bonded dimers is now justified on the basis of vibrational spectroscopy.

As a preliminary, some necessary revision to the previously published results for the $\text{In}_2\text{X}_6^{2-}$ anions is reported. Despite the earlier claim (13), it was found that these compounds dissolve in CH_3CN with only slight decomposition, and that addition of Et_2O yields good crystalline material. The vibrational spectra of these products are similar to those of the untreated materials, except that the highest frequency infrared features, at 332 cm^{-1} for Cl, 235 cm^{-1} for Br, and 186 cm^{-1} for I, have disappeared; an additional feature is also observed at 135 cm^{-1} for $\text{In}_2\text{I}_6^{2-}$. It is suggested that such absorptions are actually due to tetrahaloindate(III) anion impurities (95).

The simplified spectra of the $\text{In}_2\text{X}_6^{2-}$ anions are summarized in Table 16, from which it is clear that it is no longer necessary to invoke Fermi resonance in order to explain the spectra (cf. reference (13)). Other infrared frequencies and the Raman spectra, which remain unchanged in the newly purified materials, are not affected. These revisions must have some effect on the values of the force constants and potential energy distributions, but do not change the general conclusions reached earlier about the $\text{In}_3\text{In-InX}_3^{2-}$ structure of these anions.

Table 16. The revised infrared spectra of $\text{In}_2\text{X}_6^{2-}$ anions, as Bu_4N^+ salts (in cm^{-1})

$\text{In}_2\text{Cl}_6^{2-}$	$\text{In}_2\text{Br}_6^{2-}$	$\text{In}_2\text{I}_6^{2-}$	Assignment	Description
292s	207s	162s	E_u	$\nu(\text{In-X})$
284sh	185s	135s	A_{2u}	$\nu(\text{In-X})$

The Raman and ir features of the materials $\text{In}_2\text{X}_4\text{L}_2$ ($\text{X} = \text{Br}, \text{I}$; $\text{L} = \text{TMED}, \text{Et}_3\text{P}$) are detailed in Table 17. The most prominent feature in the spectra of each of the In_2X_4 complexes is a strong Raman line which appears at 141 cm^{-1} in $\text{In}_2\text{Br}_4(\text{TMED})_2$, at 110 cm^{-1} in $\text{In}_2\text{I}_4(\text{TMED})_2$, at 116 cm^{-1} in $\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$. These values agree well with the frequencies for $\nu(\text{In-In})$ in the corresponding anionic species $\text{In}_2\text{X}_6^{2-}$ (13), and the shift of this stretching mode with changes in net charge or coordination number follows the pattern already established for the analogous Ga_2X_4 species (88).

4.5 TRIETHYLPHOSPHINE COMPLEXES.

Once the presence of a metal-to-metal bond has been established, various ionic structures can be ruled out, but even then a number of different structural possibilities must be considered for the TMED complexes; we return to this point below. A structural formulation is most easily made in the case of $\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$. The mutual exclusion rule identifies the species as centrosymmetric, and on this basis the structure of C_{2h} skeletal symmetry shown in Figure 6 is proposed. The vibrational representation for the stretching modes of this $\text{In}_2\text{X}_4\text{P}_2$ kernel is $3\text{A}_g + \text{B}_g + \text{A}_u + 2\text{B}_u$, in which the g-modes are Raman-active and all u-modes infrared-active. It was not possible to obtain satisfactory spectra for $\text{In}_2\text{Br}_4(\text{Et}_3\text{P})_2$ (see Experimental), but the vibrational spectrum of

Table 17. Vibrational spectra of $\text{In}_2\text{X}_4\text{L}_2$ (in cm^{-1})

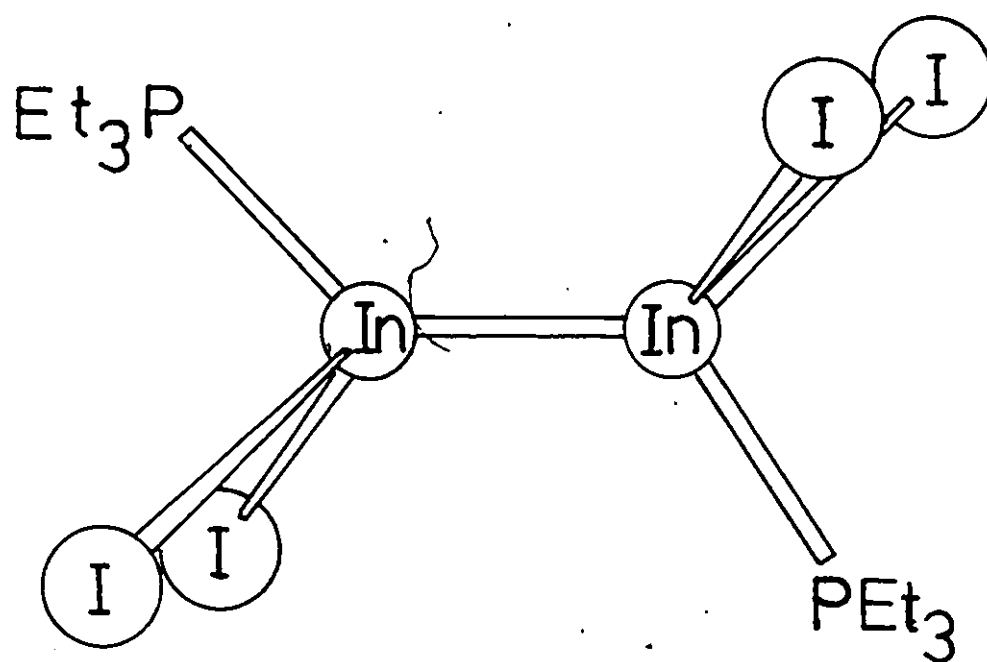
$\text{In}_2\text{Br}_4(\text{TMED})_2$ if	$\text{In}_2\text{Br}_4(\text{TMED})_2\text{C}_6\text{H}_6$ Ra	$\text{In}_2\text{I}_4(\text{TMED})_2$ Ra	$\text{In}_2\text{I}_4(\text{TMED})_2\text{C}_6\text{H}_6$ if	$\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$ Ra	Assignment (b)
488m	490m	487m	492m	486ms	(In-N)
460w, br	461w	462w	468w	466w	
440m	441vw	442m	445vw	443ms	
397vw	397w	398vw	385vw, br	380w	
362vw	368vw	367vw	362vw	354w	Unassigned
				254vw	(In-P)
				200m, br	Unassigned
210s	233vw	210s	240m	211w	(In-X)
190s, br	188w	192s, br	175w	172m	
	141s		139s	148s	
152s, br	155ah	153m, br		137m	$(A_g + B_g + A_u + B_u)$
128m	129s	128m		110s	
103m	86m	102m	86m	116s	(In-In), A_g
				106s	Bending modes
				95sh	

(a) Raman data not available

(b) All species were assigned on the basis of C_{2h} symmetry for the In_2X_4 kernel

Figure 6. Structure proposed for the adduct $\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$.

FIGURE 6



$\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$, given in Table 17, shows the $\nu(\text{In-In})$ vibration, together with bands which are reasonably attributed to the four In-I stretching modes.

The assignment of phosphorus-to-metal stretching frequencies has generally raised some difficulties.

Shobatake and Nakamoto (96) used metal isotope techniques for $\text{NiX}_2(\text{Et}_3\text{P})_2$ and thus located $\nu(\text{Ni-P})$ near 270 cm^{-1} .

The spectra of $\text{InX}_3(\text{R}_3\text{P})_2$ ($\text{X} = \text{Cl, Br or I}$; $\text{R} = \text{Me or Et}$) did not reveal any obvious $\nu(\text{In-P})$ modes (97), but a single-crystal Raman study of $\text{InCl}_3(\text{Me}_3\text{P})_2$ lead to the identification of the totally symmetric modes of this molecule, with $\nu(\text{In-P})$ being assigned at 135 cm^{-1} (98).

This frequency seems rather low in terms of mass considerations when compared to values of 307 cm^{-1} for $\nu(\text{In-Si})$ in $\text{In}(\text{SiMe}_3)_3$ (99), of $370 - 380\text{ cm}^{-1}$ for $\nu(\text{In-S})$ in a series of toluene-3,4-dithiol derivatives of indium (100), and of $319 - 339\text{ cm}^{-1}$ for this mode in $\text{InX}_3 \cdot 2\text{Et}_2\text{S}$ ($\text{X} = \text{Cl, Br}$) (71). The situation is undoubtedly complicated by the possibility of mixing modes of like symmetry. The present spectra contain bands at 376 m (ir) and 333 m cm^{-1} (Ra), shown elsewhere (96) to be $\delta(\text{CCP})$ modes of the coordinated ligand. This leaves a weak ir band at 254 cm^{-1} , which is tentatively assigned to $\nu(\text{In-P})$.

4.6 N,N,N',N'-TETRAMETHYLETHYLENEDIAMINE COMPLEXES.

In the TMED series we first consider the In-halogen stretching region, where in all cases two Raman and two

non-coincident ir features are found (Table 17). This suggests the presence of a centrosymmetric In_2X_4 unit which requires the $\text{In}_2\text{X}_4\text{N}_4$ kernel to adopt a conformation similar to that in the Et_3P analog. Inspection of the In-N stretching region, as defined by Mertz *et al.* (13) might argue against the presence of a centre of symmetry since all four features are coincident, or nearly so, but in the context of the above discussion this is attributed to a lowering of the overall molecular symmetry caused by the hydrocarbon framework of the ligand.

The frequencies of coordinated TMED have been reported previously (101), and it is assumed that the ligand is functioning as a bidentate donor in the present complexes, as implied by the presence of four $\nu(\text{In-N})$ frequencies. This requires the indium atoms in $\text{In}_2\text{X}_4(\text{TMED})_2$ to be five-coordinate, and the shift in the $\nu(\text{In-In})$ frequency from 116 cm^{-1} in $\text{In}_2\text{I}_4(\text{Et}_3\text{P})_2$ to 110 cm^{-1} in $\text{In}_2\text{I}_4(\text{TMED})_2$ is consistent with an increase in coordination number from four to five. This conclusion, and the identification of a centrosymmetric In_2I_4 unit, reveal notable differences between these indium complexes and the gallium compounds $\text{Ga}_2\text{Cl}_4(\text{dioxane})_2$, in which the dioxane is monodentate, the metal atoms are four-coordinate, and the molecular symmetry approximately C_{2h} (88).

The proposal of a five-coordinated indium-indium bonded species is not unreasonable when it is compared to isoelectronic $\text{Sn(III)} - \text{Sn(III)}$ bonded systems. The crystal

structure of $\text{Sn}_2\text{Ph}_4(\text{OAc})_2$ reveals two Ph_2Sn units linked by a metal-metal bond, and by two bridging acetate groups rendering each metal atom pentacoordinated in the solid (102). The five-coordination is maintained in solution, as revealed by vibrational spectroscopy (103).

The mode of coordination of N,N,N',N'-tetramethylethylenediamine requires some comment. As already noted, the expected bidentate coordination seems to be confirmed by the number of bands observed in the $350 - 500 \text{ cm}^{-1}$ region of the spectrum ($\nu(\text{In-N})$). This still leaves at least three possibilities to consider: a) terminal TMED, b) intermolecular bridging, and c) intramolecular bridging. The second possibility can be rejected in view of the results for the $700 - 900 \text{ cm}^{-1}$ region of the infrared spectrum. Chelate-type diamines display two bands, assigned as CH_2 rocking vibrations at approximately 810 and 770 cm^{-1} , while intermolecular bridging leads to a *trans* conformation in the diamine, with ir bands at 870 and 790 cm^{-1} (93, 101). The materials under discussion show bands at 770w and 790s , implying a *cis* or *gauche* conformation of bidentate TMED, and the structures are accordingly written as $\text{X}_2(\text{TMED})\text{InIn}(\text{TMED})\text{X}_2$.

Some spectral features still remain unexplained after this analysis. Several of these can be ascribed to small amounts of impurities, as is the case of $\text{In}_2\text{Br}_4(\text{TMED})_2\text{C}_6\text{H}_6$ where a Raman line at 197 cm^{-1} , and an ir feature at 236 cm^{-1} point to the presence of InBr_4^- . Perhaps of more interest is the strong Raman line found at 129 cm^{-1}

in the spectrum of $\text{In}_2\text{Br}_4(\text{TMED})_2$. The intensity and position of this feature suggest the presence of a second metal-metal bonded species, with the frequency of this vibration affected either by a higher coordination number or by an increase of negative charge, or both. As can be seen from Table 15, the analyses for this material do not agree particularly well with the presumed composition, so that the presence of some unidentified second compound in the crude material is not unreasonable. The present interpretation has also neglected the presence of bending modes which will be responsible for some of the features still unexplained in the assignments in Table 17.

4.7 REACTION PATHWAY.

Although the reaction is apparently the single addition of neutral ligand to indium dihalide, two significant factors must be recognized. The first is that few of the InX_2^- ligand combinations investigated do in fact yield the desired product, and that in most cases disproportionation to In^0 and presumably In^{III} species predominates. The second is that a deep-red or orange colour is formed on the addition of either anionic (13⁺) or neutral ligands (this work) to solutions of indium dihalide, which is compatible with the establishment of the equilibrium $\text{In}_2\text{X}_4 \rightleftharpoons \text{InX} + \text{InX}_3$. Since very little is known about the solution chemistry of indium(I) or indium(II) compounds in aromatic solvents, these various observations cannot be

rationalized at the present time.

4.8 CONCLUSIONS.

The reaction of indium dihalides and some selected ligands proceeds with formation of metal-metal bonds. In this context, the behaviour of the dihalides is different, when compared to their pattern of interaction with bulky macrocycles.

The factors governing this difference in behaviour, and those leading to disproportionation, are not clearly understood at the present time.

CHAPTER 5

SYNTHETIC APPROACHES TO SOME LOW VALENT ORGANOINDIUM COMPOUNDS

5.1 INTRODUCTION

The organic chemistry of low valent oxidation states in the Main Group III is restricted to a handful of reports dealing with less than a dozen compounds, some of them only partly characterized.

Among the lighter elements in the group, there are only two examples to be considered. The reaction of $(i\text{-Bu})_3\text{Al}$ with potassium metal affords a brown material of composition $\text{KAl}(i\text{-Bu})_3$, for which the proposed structure is an ionic dimer incorporating metal-metal bonds (104, 105). Similar reactions carried out with $(i\text{-Bu})_2\text{AlCl}$ and potassium yielded the dimer $(i\text{-Bu})_2\text{Al}_2(i\text{-Bu})_2$, also containing a metal-metal bond (106, 107).

Monovalent gallium derivatives, obtained through the reaction scheme $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 + \text{MH} \longrightarrow \text{SiMe}_4 + \text{MGa}(\text{CH}_2\text{SiMe}_3)_2$ ($\text{M} = \text{Na}, \text{K}$) were recently reported. Molecular weight determinations showed that the potassium derivative is dimeric in benzene, while the sodium analogue is trimeric. The association was ascribed to Ga-M-Ga bridging, and spectral properties were consistent with this formulation (108). Indium analogues were also synthesized by the same route (109).

It has been reported that the reaction of Me_3Ga and Me_2GaCl with sodium in liquid ammonia leads to the formation of the extremely unstable species $\text{Na}_2\text{Ga}_2\text{Me}_6$ and $(\text{Me}_2\text{Ga}:\text{NH}_3)_2$

respectively, although no conclusive evidence was presented in favor of the structures proposed (110). Related experiments involved reduction of trimethylgallium and thallium with potassium in 1,2-dimethoxyethane. These experiments were said to produce the salts $K_2M_2Me_6$ ($M = Ga, Tl$) (60). Again, one can only regret the absence of spectroscopic studies on these materials.

The best characterized series of compounds involving low oxidation states in the Main Group III is the one spanned by the general formulation MR ($M = In, Tl$; $R = C_5H_5, MeC_5H_4$), although it is as well to point out that some controversy has surrounded the problem of the metal-to-ring interaction in these compounds. This topic was reviewed elsewhere (111).

Cyclopentadienylindium(I) was first prepared from $InCl_3$ and an excess of cyclopentadienylsodium (18). The synthetic approach was later the subject of studies where conditions were established for the selective isolation of InC_5H_5 or its precursor $In(C_5H_5)_3$. According to the same report (22), a similar procedure was used to make $In(C_5H_4Me)$. More recently, Russian workers succeeded in preparing InC_5H_5 by the co-condensation of the metals and cyclopentadiene (112).

The structure of solid InC_5H_5 features a polymeric array in which the metal atom is sandwiched between two cyclopentadienyl rings, located at 3.19 \AA from the metal center (113). The vapour phase structure of this compound consists of monomeric half sandwiches of precise C_{5v} symmetry, the metal-ring perpendicular distances being 0.8 \AA shorter than in the solid state structure, indicating an increase of covalency of the metal-ring interaction in the gas phase (114).

This Chapter describes several experiments aimed at the characterization of novel low valent organoindium compounds. The results do not supply any firm conclusion on the problem, but can perhaps help in designing other and more successful experiments.

5.2 EXPERIMENTAL

Starting Materials: Triphenylindium was prepared by a simple modification of the procedure followed by Gilman and Jones (16), which consists in refluxing 6.0 g (52.4 mMol) of the metal (Alfa, tear drop) with 20 g (56.4 mMol) of diphenylmercury (Alfa) in 250 mL of a mixture of isomeric xylenes (137-140°bp). After 72 hrs, the heavy liquid amalgam of Hg/In produced was allowed to settle, and the solution, at 100°C, was decanted into another vessel. On cooling, white needles of InPh_3 were produced. These were filtered, washed with 50 mL of light ligroin (40-60°bp) and dried. Yields were 60 to 80% based on diphenylmercury.

Reduction of organoindium(III) species

a) 1.0 g (2.9 mMol) of InPh_3 and equimolar amounts of sodium strip were suspended in 30 mL of toluene and refluxed for 14 hrs. The gray suspension was filtered off and Soxhlet extracted with 120 mL of benzene during 4 hrs. After cooling, the residual hard crust of gray solid was triturated and extracted again. This procedure was repeated to a total extraction time of 72 hrs. The benzene suspension was filtered, and the white solid dried to yield 0.8 g of NaInPh_4 . The gray residue insoluble in benzene (0.115 g) had the composition 96.5% In, by analysis.

Table 18. Analytical Results for Some Organoindium(III) Compounds

	Found %			Required (%)		
	In	Na	Halogen	In	Na	Halogen
NaInPh ₄	25.6	5.1		25.8	5.2	
MeInO	78.6			78.8		
Me ₂ InCl	63.9		20.0	63.7		19.7
Bu ₄ N InPh ₃ Cl	18.4	3.9	5.7	18.4	3.7	5.7
Bu ₄ N InPh ₄	17.1	3.5		17.3	3.5	
Ph ₂ InI	28.6		32.3	29.0		32.1
Me ₃ In ₂ I ₃	35.3		58.5	35.1		58.1
InC ₅ H ₅	63.5			63.9		

b) 1.53 g (4.42 mMol) of InPh_3 was deposited in a Schlenk flask and after evacuation 20 to 30 mL of ammonia was condensed by cooling the flask with liquid nitrogen. The system was allowed to reach the boiling point of ammonia (-30 to -40°); when dissolution of InPh_3 was observed. The bath of liquid nitrogen was replaced and 0.102 g (4.43 mMol) of sodium strip added. The cooling bath was again removed and as soon as the melting of the solvent allowed, stirring was started. A vigorous reaction occurred, during which the dark blue colour of Na/NH_3 discharged, to yield a light brown solid suspended in a yellow solution. Ammonia was allowed to evaporate, and as the system reached room temperature, the non volatile phase rapidly darkened to yield a gray-brown mass, which proved to be insoluble in Et_2O , THF or 1,4-dioxane. Addition of acetone, acetonitrile or ethanol immediately deposited indium metal. Soxhlet extraction in benzene yielded NaInPh_4 and indium metal, as in the previous experiment. In similar runs, where the molar ratio Na/InPh_3 was varied between 1.1 and 2.0, the blue colour of sodium in ammonia failed to discharge over a period of 3 hours.

c) 5.075 g (18.7 mMol) of dimethylindium iodide and equimolar amounts of sodium (0.429 g) were suspended in 100 mL of toluene and refluxed for 3 hours. The gray precipitate was filtered and washed with three 50 mL portions of hot toluene, dried and taken up in 125 mL of hot ethanol, to give a black lustrous powder, which was separated by filtration (0.735 g, 98.5% In by analysis). The ethanol solution was evaporated to

dryness to yield 2.738 g of NaI (84.6 % I by analysis). The toluene solution was evaporated to dryness, condensing the volatile phase in liquid nitrogen. Traces (approx. 75 mg) of unreacted Me_2InI were recovered. The presence of volatile Me_3In in the toluene solution was confirmed by two experiments: (i) vigorous aeration to yield MeInO and (ii) solvolysis with methanol, followed by reaction with an ethanol solution of HCl to give Me_2InCl .

d) 1.00 g (5.54 mMol) of Me_2InCl and equimolar amounts (0.128 g) of sodium were reacted in liquid ammonia, in the same way as for InPh_3 . The blue color rapidly discharged to form a light orange suspension. On evaporation of the solvent, rapid decomposition occurred, as evidenced by the gray appearance of the solid material. This experiment was not pursued any further.

Alkylation and arylation of indium(II) derivatives.

a) 1.53 g (1.65 mMol) of crude $(\text{Bu}_4\text{N})_2\text{In}_2\text{Cl}_6$ (contaminated with InCl_4^- , see Chapter 4) was suspended in 50 mL of diethyl ether, and cooled to $\text{CO}_2/\text{acetone}$ temperature. 10 mMol (4.3 mL of a 2.3 M solution) of phenyllithium in diethyl ether was added dropwise, and the mixture stirred for 3 hrs. At this stage the cooling was discontinued and stirring maintained for three more hours, when the suspension progressively became gray. This was filtered and weighted, accounting for 93% of all the material put in. A strong smell of free amine was evident in the diethyl ether solution. The gray solid was extracted with 100 mL of hot benzene, the insoluble residue was filtered off and the solution of benzene was cooled. A white crystalline material was given off. This was filtered and dried to yield

0.35 g of $\text{Bu}_4\text{N InPh}_3\text{Cl}$: Further extraction with benzene yielded amorphous $\text{Bu}_4\text{N InPh}_4$. When the experiment was repeated using $\text{In}_2\text{Cl}_6^{2-}$ free from InCl_4^- , only $\text{Bu}_4\text{N InPh}_4$ was obtained.

b) 1.50 g (1.92 mMol) of $\text{In}_2\text{Br}_4(\text{TMED})_2$ was dissolved in 125 mL of benzene and the solution was cooled with a CO_2 /acetone bath. A fourfold molar excess of methyllithium in ether was added with stirring. An immediate reaction was evident, with formation of a chocolate-brown precipitate. During subsequent filtration, the temperature of the system reached -15° , at which point a rather fast decomposition to indium metal was observed. The experiment was not pursued.

Comproportionation of organoindium(III) species and indium(I) iodide.

a) 1.15 g (3.32 mMol) of InPh_3 and an equimolar amount (0.804 g) of InI were refluxed for 4 hrs. in 100 mL of toluene. The gray suspension was filtered off to yield 0.191 g of indium metal (94 % In). The solution was evaporated to 50 mL at which point a powdery off-white material was given off. This was filtered and dried to yield 0.75 g of Ph_2InI .

b) 2.15 g (7.90 mMol) of Me_2InI and equimolar amounts (1.912 g) of InI were refluxed in 100 mL of toluene for 3 hrs. The gray suspension produced was filtered while hot to yield 0.59 g of indium metal (98 % In). After cooling, the mother liquors gave a white precipitate of composition $\text{Me}_3\text{In}_2\text{I}_3$. The experiment was repeated adding 16.0 mMol of TMED. After 30 min. of stirring at room temperature, the gray colour of indium metal was again evident. No efforts were made to identify the species in solution.

Salt displacement from indium(I) halides and organolithium compounds.

a) 1.55 g (10.3 mMol) of indium(I) chloride and a five-fold molar excess of cyclopentadienyllithium were suspended in 100 mL of diethyl ether and the mixture stirred at room temperature for twelve hours. The solvent was stripped off to give an off-white solid, which was sublimed at 100° for one hour, to give 1.34 g (72 % yield, based on InCl) of cyclopentadienylindium(I). Small losses (less than 5 %) of product occurred during evaporation of the solvent and subsequent sublimation.

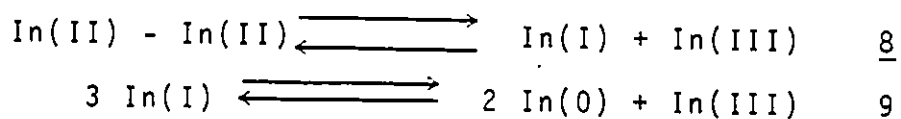
b) 2.0 g (10.3 mMol) of indium(I) bromide were suspended in 100 mL of diethyl ether and the suspension cooled at CO₂/acetone temperature. Equimolar amounts of an indenyllithium solution in ether were added while stirring. Immediate development of a brown colour was evident. After the addition was completed, stirring was maintained for two hours at low temperature. At this stage all the indium(I) bromide had dissolved, and the cooling bath was removed. As the system reached room temperature, the deposition of gray indium metal was evident and the colour of the solution changed from deep brown to light yellow. The metal was collected (0.75 g). Isolation of the material in solution was not attempted.

5.3 GENERAL

From the experimental results described above, the reduction to indium metal is a general trend observed in all the systems studied so far, except for the InCl/NaC₅H₅ case, discussed below. It is believed that such reduction is part

of a disproportionation process suffered by the unstable low valent intermediates. Such behavior would be quite in agreement with the results obtained from the reaction of indium dihalides and neutral ligands, in which most of the systems under study undergo similar disproportionation (cf. Chapter 4).

On the basis of the limited number of experiments which have actually afforded indium(II) - indium(II) bonded compounds (cf. Chapter 4), one can only make a tentative attempt to identify the factors affecting the stability of the metal - metal bond in these systems. For the sake of simplicity, such discussions are most easily based on the anionic $\text{In}_2\text{X}_6^{2-}$ and neutral $\text{In}_2\text{X}_4\text{L}_2$ complexes of indium(II) ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{L} = \text{TMED}, \text{Et}_3\text{P}$), rather than the organoindium(II) derivatives studied during the course of this work. The aim of the remainder of this section is to advance the proposal that disproportionation of $\text{In(II)} - \text{In(II)}$ compounds, which must involve rupture of the metal - metal bond, is then followed by a second disproportionation of the relevant indium(I) species.



Force constants of the In - In stretchings in the series $\text{In}_2\text{X}_6^{2-}$ are consistent with a general order of metal - metal bond strength given by $\text{Cl} > \text{Br} > \text{I}$. Similar conclusions can be drawn from the ^{115}In -NMR studies of solutions of these materials in acetonitrile (cf. Chapter 2). Preparative evidence related to the synthesis of the hexahaloindate(II) anions, on the other hand, suggests that disproportionation becomes easier as the atomic number of the halogen decreases. This

also holds true for the series of neutral indium(II) adducts, to the extent that no chloro derivatives have been isolated in this case (cf. Chapter 4).

These various observations can be reconciled if the following is valid:

- 1) the position of equilibrium 8 is progressively shifted to the right along the series $\text{Cl} < \text{Br} < \text{I}$
- 2) the rate of disproportionation in equation 9 varies according to $\text{Cl} > \text{Br} > \text{I}$

In these conditions, the observed rate of appearance of indium metal would be determined by factor (2). More importantly, the formation of $\text{In(II)} - \text{In(II)}$ compounds will be prevented if eq. 9 is the dominant process.

Preparative studies not described in this Thesis (by C. Peppe), indicate that $\text{In(I)}/\text{Cl}$ systems afford indium metal with considerable more ease than do the related bromide or iodide systems (115), thus supporting the above argument. In any case, equilibrium 9 is displaced well to the right, judging from the values of the relevant equilibrium constants in aqueous solution [$K_{\text{Ga}} = 10^{19}$, $K_{\text{In}} = 10^{12}$ (82)].

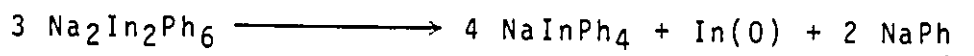
In the absence of additional pertinent information, the foregoing analysis gives support to the contention that indium(II) systems decompose via indium(I) intermediates.

5.4 REDUCTION OF ORGANOINDIUM(III) SPECIES

The production of indium metal in those experiments involving high boiling point solvents is not surprising. The reduction of trialkyl (116, 117) and triaryl (118) indium

compounds with alkali metals has been used as a route to the preparation of tetraorganoindate(III) anions. Also, reduction of indium trichloride with potassium in xylenes has afforded a method for the preparation of highly reactive indium powder (119, 120). However, the existence of short lived low valent intermediates in these reduction processes cannot be discounted.

The experiments involving liquid ammonia as a solvent are more complex. Firstly, it should be noted that, regardless of the solvent used in the reduction, disproportionation occurs on raising the temperature. It cannot be ascertained at this point whether this decomposition is also associated to the loss of ammonia. At low temperature, the stoichiometry of the reaction, as determined by addition of an excess of sodium, indicates that the main process is a one - electron reduction of triphenylindium, presumably in the form of its ammonia adduct. This is consistent with the formation of a radical anion $\cdot\text{InPh}_3^-$, or more likely its metal - metal bonded dimer $\text{In}_2\text{Ph}_6^{2-}$, which could then disproportionate according to



Indeed, such stoichiometry has been determined experimentally, by weighing the metal produced (see Experimental). The product NaInPh_4 has been reported previously and a crystal structure determination has established the tetrahedral disposition of the phenyl groups about the metal centre (118). The ir and Raman spectra recorded for this material agree with the published data (118).

5.5 ALKYLATION AND ARYLATION OF INDIUM(II) COMPOUNDS

Again, the experimental observations point at the existence of unstable intermediate species at low temperature, with irreversible disproportionation taking place as the systems reach room temperature. If these intermediates are the metal - metal bonded $\text{In}_2\text{Ph}_6^{2-}$ and $\text{In}_2\text{Me}_4(\text{TMED})_2$, it is possible to postulate a mechanism whereby the (local) excess of organolithium reagent can attack the metal center, with further splitting of the indium - indium bond.

It is tempting to attribute the formation of the anion Ph_3InCl^- to a mechanism similar to the above, involving nucleophilic attack of Cl^- on the intermediate $\text{In}_2\text{Ph}_6^{2-}$, but since the triphenylchloroindate(III) anion only occurs in those systems contaminated with InCl_4^- , it must arise either through direct organylation of the latter species, or by redistribution from InCl_4^- and InPh_4^- .

One more point arises in connection with the attempted phenylation of $(\text{Bu}_4\text{N})_2\text{In}_2\text{Cl}_6$. According to the foregoing discussion, the stoichiometry of the overall reaction should be:

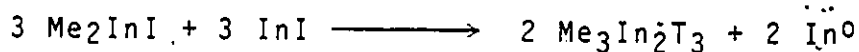
$$3 (\text{Bu}_4\text{N})_2\text{In}_2\text{Cl}_6 + 18 \text{PhLi} \longrightarrow 18 \text{LiCl} + 4 \text{Bu}_4\text{N InPh}_4 + (2 \text{Bu}_4\text{N Ph?})$$

The existence of $\text{Bu}_4\text{N Ph}$ is extremely doubtful, and the actual solution phase probably consists of Bu_3N and BuPh , produced by nucleophilic attack of the strong base Ph^- on the α - carbon of the tetra-n-butylammonium cation. In support of this, a characteristic smell of free amine was detected in the diethyl ether reaction solution.

5.6 COMPROPORTIONATION OF ORGANOINDIUM(III) SPECIES AND INDIUM(I) IODIDE

Two additional lines of argument need to be quoted in connection with these attempts to make low valent indium derivatives. First, we note that the reaction of indium triiodide and indium monoiodide in aromatic solvents lead to formation of indium diiodide, formulated as $\text{In}^+\text{InI}_4^-$ (11). It was then conceivable that species of composition R_3In and R_2InI could undergo similar reactions to yield $\text{In}^+\text{R}_3\text{InI}^-$ and $\text{In}^+\text{R}_2\text{InI}_2^-$ respectively. On the other hand the presence of TMED in the system $\text{InI}_3/\text{aromatic solvent}/\text{InI}$, lead to stabilization of the metal - metal bonded species, according to the experiments described in section 4.7, so that we might expect similar results in the system $\text{Me}_2\text{InI}/\text{InI}/\text{TMED}/\text{toluene}$.

Again, the main process in these experiments is the disproportionation of indium. This cannot involve indium iodide only, since this material is known to be stable under similar experimental conditions. On this basis, it is believed that comproportionation occurs, to form the species $\text{In}^+\text{InPh}_3\text{I}^-$ and $\text{In}^+\text{InMe}_2\text{I}_2^-$ in those experiments which do not involve donor ligands. These materials could then disproportionate to yield indium metal and the organoindium halides Ph_2InI and $\text{Me}_3\text{In}_2\text{I}_3$ according to the overall equations:



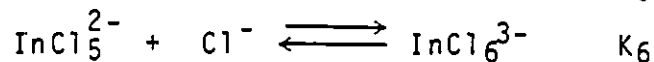
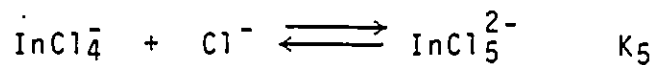
The species $\text{Me}_3\text{In}_2\text{I}_3$ was reported in the reaction of Me_2InI with MeInI_2 (14) and also in the oxidation of indium metal with methyl iodide (171). Species of the general formula $\text{Me}_n\text{In}_2\text{I}_{6-n}$ ($n = 0, \dots, 6$) are related to each other by complex equilibria (14).

5.7 REACTIONS OF INDIUM(I) HALIDES AND ORGANOLITHIUM COMPOUNDS

The production of cyclopentadienylindium(I) from monovalent indium halides is surprising, since the usual pattern of reaction of InX (X = halogen) with methyllithium and phenyllithium involves disproportionation (115) in the same way as the $\text{LiC}_9\text{H}_7/\text{InBr}$ system described in section 5.2 (C_9H_7 = indenyl). On this basis, it seems that disproportionation is also the dominant feature in systems involving organoindium (I) compounds, unless some unusual stabilizing factor is incorporated in the structure. Such is the case for InC_5H_5 . Solid state (113) and vapour phase (114) diffraction studies on this compound have established that the ring is pentahapto, supplying a total of five electrons to the metal-ring bond, so that the metal is surrounded by a stable electronic octet (122). In this context, the indenyl ligand has to be considered a sigma, one electron donor, since the electron density is largely delocalized over the fused six membered aromatic ring. Accordingly, no indenyl derivatives displaying a pentahapto bonding pattern have been reported in Main Group chemistry.

APPENDIX A - THE SYSTEM $\text{InCl}_4^-/\text{Cl}^-$

Consider the simultaneous equilibria



Both equilibrium constants can be combined to give

$$\frac{K_6}{K_5} = \frac{y (A - x - y)}{x^2}$$

where A: initial concentration of InCl_4^- = total concentration of indium

x: concentration of InCl_5^{2-}

y: concentration of InCl_6^{3-}

B: concentration of added chloride

Solving for x

$$x = \frac{K_5}{2 K_6} \left[-y + \sqrt{1 - \frac{4 K_6}{K_5} + \frac{4 K_6 A}{K_5 y}} \right]$$

Assuming that $K_5/K_6 \gg 1$, the binomial theorem gives

$$x \sim \frac{K_5}{2 K_6} \left[y + \frac{2 A K_6}{K_5} - \frac{2 y K_6}{K_5} \right]$$

The expression for the experimental chemical shift

$$\delta_E = \frac{1}{A} [(A - x - y)\delta_4 + x \delta_5 + y \delta_6]$$

can be transformed to

$$\delta_E = \delta_5 + (\delta_6 - \delta_5) \frac{y}{A}, \text{ since } \delta_4 = 0 \text{ (by definition)}$$

and $x = A - y$. When δ_E is plotted as a function of B (Figure 5), the slope of the curve is given by

$$\frac{\Delta \delta_E}{\Delta B} = \frac{\delta_5}{A}. \text{ This results in } \delta_5 = 115.5 \text{ ppm}$$

As suggested by Figure 5, δ_6 should be in the order of 200 to 240 ppm. Different δ_6 values are tried, so as to give a constant K_6 in the range $0.25 < B < 0.45$. The best fit is obtained for the values $\delta_6 = 235$ ppm, and $K_6 = 10$.

Finally, the ratio K_6/K_5 is varied, to fit a calculated chemical shift (solid trace in Figure 5). The best fit gives $K_6/K_5 = 0.02$.

REFERENCES

- (1) A.J. Carty and D.G. Tuck, *Prog. Inorg. Chem.*, 1975, 19, 245
- (2) D.G. Tuck, *MTP International Rev. Sci., Inorg. Chem., Series 2*, Vol. 1 (M.F. Lappert, Ed.), 1975, 311.
- (3) T. Tanaka, *J. Organomet. Chem.*, 1980, 180, 65.
- (4) D.G. Tuck, Comprehensive Organometallic Chemistry, Vol. 1, Chapter 7, (E. Abel, F.G.A. Stone and G. Wilkinson, Ed.), Pergamon, to be published.
- (5) F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Ed., Interscience, New York, 1972.
- (6) R.J. Gillespie, *J. Chem. Ed.*, 1970, 47, 18.
- (7) L.S. Bartell, *J. Chem. Ed.*, 1968, 45, 754.
- (8) R.F. Zahrobsky, *J. Amer. Chem. Soc.*, 1971, 93, 3313.
- (9) D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, 2nd Ed., Penguin, New York, 1980.
- (10) A.J. Carty and D.G. Tuck, *J. Chem. Soc., A*, 1966, 1081.
- (11) B.H. Freeland and D.G. Tuck, *Inorg. Chem.*, 1976, 15, 475.
- (12) A.F. Berniaz, Ph.D. Thesis, Simon Fraser University, 1973.
- (13) B.H. Freeland, J.L. Hencher, D.G. Tuck and J.G. Contreras, *Inorg. Chem.*, 1976, 15, 2144.
- (14) J.S. Poland and D.G. Tuck, *J. Organomet. Chem.*, 1972, 42, 315
- (15) H.C. Clark and A.L. Pickard, *J. Organomet. Chem.*, 1967, 8, 427.
- (16) H. Gilman and R.G. Jones, *J. Amer. Chem. Soc.*, 1940, 62, 2353.
- (17) W.C. Schumb and H.I. Crane, *J. Amer. Chem. Soc.*, 1938, 60, 306
- (18) E.O. Fischer and H.P. Hofmann, *Angew. Chem.*, 1957, 69, 639
- (19) J.J. Habeeb and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1976, 866.

- (20) R.J. Clark, E. Griswold and J. Kleinberg, J. Amer. Chem. Soc., 1958, 80, 4764.
- (21) D. J. Gislason, M.H. Lloyd and D.G. Tuck, Inorg. Chem., 1971, 10, 1907.
- (22) J.S. Poland and D.G. Tuck, J. Organomet. Chem, 1972, 42, 307.
- (23) K.L. Brown and D. Hall, J. Chem. Soc., Dalton Trans., 1973, 1843.
- (24) B.F.G. Johnson and R.A. Walton, Inorg Chem., 1966, 5, 49.
- (25) R.A. Walton, Inorg. Chem., 1968, 7, 640.
- (26) R.A. Walton, Inorg. Chem., 1968, 7, 1927.
- (27) J.E.D. Davies and D.A. Long, J. Chem. Soc., A, 1968, 2050.
- (28) R.W. Matthews and R.A. Walton, J. Chem. Soc., A, 1968, 1639.
- (29) J.J. Habeeb, F.S. Said and D.G. Tuck, J. Organomet. Chem., 1980, 190, 325.
- (30) J.J. Habeeb and D.G. Tuck, J. Chem. Soc., Dalton Trans., 1975, 1815.
- (31) J.E. Drake, J.L. Hencher, L.N. Khasrou, D.G. Tuck and L. Victoriano, Inorg. Chem., 1980, 19, 34.
- (32) D.G. Tuck, Proc. CNRS Conference No. 191, Editions du CNRS, Paris, 1970.
- (33) D.H. Hague and R.H. Prince, J. Inorg. Nucl. Chem., 1966, 28, 1039.
- (34) G. Tagliavini, S. Faleschini, G. Pilloni and G. Planzzongna, J. Organomet. Chem., 1966, 5, 136.
- (35) K. Ziegler, L. Ewald and P. Orth, Ann., 1930, 479, 277.
- (36) A. Takita, M. Kumada and K. Tarama, Nippon Kagaku Zasshi, 1957, 78, 999.

- (37) J. Widler, H.D. Hausen and J. Weidlein, Z. Naturforsch., 1975, 30, 645.
- (38) L.A. Woodward and M.J. Taylor, J. Chem. Soc., 1960, 4473.
- (39) L.A. Woodward and P.T. Bill, J. Chem. Soc., 1955, 1699.
- (40) L.A. Woodward and G.H. Singer, J. Chem. Soc., 1958, 716
- (41) J.G. Contreras and D.G. Tuck, Inorg. Chem., 1972, 11, 2967.
- (42) A.G. Maki and R. Forneris, Spectrochim. Acta., 1967, 23 A, 1967.
- (43) J.G. Contreras, T.J. O'Connor and D.G. Tuck, unpublished results.
- (44) T.H. Cannon and R.E. Richards, J. Chem. Soc., Faraday Trans., 1966, 62, 1378.
- (45) A. Fratiello, D.D. Davis, S. Peak and R.E. Schuster, Inorg. Chem., 1971, 10, 1627.
- (46) H. Haraguchi, K. Fuwa and S. Fujiwara, J. Phys. Chem., 1973, 17, 1497.
- (47) J.F. Hinton and R.W. Briggs, NMR and the Periodic Table, (R.K. Harris and B.E. Mann, Ed.), Academic Press, London, 1978.
- (48) J. Trotter, F.W.B. Einstein and D.G. Tuck, Acta Cryst., 1969, B25, 603.
- (49) M. Khan and D.G. Tuck, Unpublished results
- (50) F.W.B. Einstein and D.G. Tuck, Chem. Commun., 1970, 1182
- (51) J.D. Forrester, A. Zalkin and D.H. Templeton, Inorg. Chem., 1964, 3, 63.
- (52) D.S. Brown, F.W.B. Einstein and D.G. Tuck, Inorg. Chem., 1969, 8, 14.

- (53) G. Joy, A.P. Gaughan, I. Wharf, D.F. Shriver and T.A. Dougherty, *Inorg. Chem.*, 1975, 14, 1795.
- (54) D.F. Shriver and I. Wharf, *Inorg. Chem.*, 1969, 8, 2167.
- (55) J.G. Contreras, F.W.B. Einstein, M.M. Gilbert and D.G. Tuck, *Acta Cryst.*, 1977, B 33, 1648.
- (56) B.H. Freeland, J.J. Habeeb and D.G. Tuck, *Can. J. Chem.*, 1977, 55, 1527.
- (57) R.G. Kidd and D.R. Truax, *J. Amer. Chem. Soc.*, 1968, 90, 6867.
- (58) J.J. Burke and P.C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, 83, 326.
- (59) B.R. McGarvey, M.J. Taylor and D.G. Tuck, *Inorg. Chem.*, 1981, 20, 2010.
- (60) G.E. Coates and K. Wade, Organometallic Compounds, Vol. 1, The Main Group Elements, Methuen, London, 1967.
- (61) J.G. Contreras, J.S. Poland and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1973, 922.
- (62) P.L. Goggin and I.J. McColm, *J. Inorg. Nucl. Chem.*, 1966, 28, 2501.
- (63) A.P. Kochetkova, V.G. Tronev and V.N. Gilyarov, *Doklady Akad.Nauk SSSR*, 1962, 147, 1086.
- (64) L. Waterworth and I.J. Worrall, *Inorg. Nucl. Chem. Lett.*, 1972, 8, 123.
- (65) P.J. Davidson, D.H. Harrison and M.F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.
- (66) R. Guillard, P. Cocolios and P. Fournari, *J. Organomet. Chem.*, 1977, 129, C 11.
- (67) M.E. Farago, *Inorg. Chim. Acta*, 1977, 23, 211.

- (68) E.J. Bounsall and S.R. Koprach, Can. J. Chem., 1970, 48, 1481.
- (69) R.E. Hester and R.A. Plane, Inorg. Chem., 1964, 3, 513.
- (70) M.J. Taylor, J. Chem. Soc., A, 1967, 1462.
- (71) C.A. Evans and M.J. Taylor, J. Chem. Soc., A, 1969, 1343.
- (72) A.J. Carty and H.A. Patel, Can. J. Chem., 1970, 48, 492.
- (73) K. Mertz, W. Schwartz, B. Eberwein, J. Weidlein, H. Hess and H.D. Hausen, Z. Anorg. Chem., 1977, 429, 99.
- (74) F.J. Brinkmann and H. Gerding, Inorg. Nucl. Chem. Lett., 1970, 6, 801.
- (75) R.H. Herber and A.E. Smelkinson, Inorg. Chem., 1978, 17, 1023.
- (76) J.E. Davies and D.A. Long, J. Chem. Soc., A 1968, 2054.
- (77) W. Klemperer, J. Chem. Phys., 1956, 25, 1066.
- (78) A.J. Carty and D.G. Tuck, J. Chem. Soc., 1964, 6012.
- (79) M.J. Taylor, D.G. Tuck and L. Victoriano, J. Chem. Soc., Dalton Trans, 1981, 928.
- (80) J.G. Contreras and D.G. Tuck, Chem. Commun., 1971, 1552.
- (81) J.J. Habeeb and D.G. Tuck, Chem. Commun., 1975, 600.
- (82) M.J. Taylor, Metal To Metal Bonded States of the Main Group Elements, Academic Press, New York, 1975:
- (83) C.A. Evans, K.H. Tan, S.P. Tapper and M.J. Taylor, J. Chem. Soc., Dalton Trans., 1973, 988.
- (84) H.J. Cumming, D. Hall and C.E. Wright, Cryst. Struct. Comm., 1974, 3, 107.
- (85) M. Khan, C. Oldham, M.J. Taylor and D.G. Tuck, Inorg. Nucl. Chem. Lett., 1980, 16, 469.

- (86) W. Lind, L. Waterworth and I.J. Worrall, Inorg. Nucl. Chem. Lett., 1971, 7, 611.
- (87) L.G. Waterworth and I.J. Worrall, J. Inorg. Nucl. Chem., 1973, 35, 1535.
- (88) J.C. Beamish, R.W.H. Small and I.J. Worrall, Inorg. Chem., 1979, 18, 220.
- (89) J.H.R. Clark and R.E. Hester, Inorg. Chem., 1969, 8, 1113.
- (90) I. Waterworth and I.J. Worrall, Inorg. Nucl. Chem. Lett., 1972, 8, 123.
- (91) A.P. Kochetkova and O.N. Gilyarov, Russ. J. Inorg. Chem., 1966, 11, 662.
- (92) I.J. Worrall to D.G. Tuck, 1981, personal communication
- (93) K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, J. Wiley, New York, 1969.
- (94) J.H.S. Green, Spectrochim. Acta, 1968, 24 A, 137.
- (95) D.M. Adams, Metal - Ligand and Related Vibrations, E. Arnold, London, 1967.
- (96) K. Shobatake and K. Nakamoto, J. Amer. Chem. Soc., 1970, 92, 3332.
- (97) A.J. Carty, T. Hinsperger and P.M. Boorman, Can. J. Chem., 1970, 48, 1959.
- (98) G.A. Ozin, J. Chem. Soc., A, 1970, 1307
- (99) H. Burger and V. Goetze, Angew. Chem., Int. Ed., 1969, 8, 140.
- (100) D.G. Tuck and M.K. Yang, J. Chem. Soc., A, 1971, 214.
- (101) L. Maresca, G. Natile and G. Rizzardi, Inorg. Chim. Acta, 1980, 38, 53.
- (102) G. Bandoli, D.A. Clemente and C. Panattoni, Chem. Commun.,

- 1971, 311.
- (103) G. Plazzogna, W. Peruzzo and G. Tagliavini, J. Organomet. Chem., 1970, 24, 667.
- (104) H. Hoberg and S. Krause, Angew. Chem., 1978, 90, 1013.
- (105) H. Hoberg and S. Krause, Angew. Chem., Int. Ed., 1978, 17, 949.
- (106) H. Hoberg and S. Krause, Angew. Chem., 1976, 88, 760.
- (107) H. Hoberg and S. Krause, Angew. Chem., Int. Ed., 1976, 15, 694.
- (108) O.T. Beachley and R.G. Simmons, Inorg. Chem., 1980, 19, 3042.
- (109) O.T. Beachley and R.N. Rusinko, Inorg. Chem., 1981, 20, 1367.
- (110) C.A. Kraus and F.E. Toonder, J. Amer. Chem. Soc., 1933, 55, 3547.
- (111) A.A. Koridze, N.A. Ogorodnikova and P.V. Petrovsky, J. Organomet. Chem., 1978, 157, 145.
- (112) G.M. Kuz'yants, Izv. Akad. Nauk SSSR, Ser. Khim., 1976, 1895.
- (113) E. Frasson, F. Menegus and C. Panattoni, Nature, 1963, 199, 1087.
- (114) S. Shibata, L.S. Bartell and R.M. Gavin, J. Chem. Phys., 1964, 41, 717.
- (115) C. Peppe, D.G. Tuck and L. Victoriano, unpublished results.
- (116) K. Hoffmann and E. Weiss, J. Organomet. Chem., 1972, 37, 1.
- (117) K. Hoffmann and E. Weiss, J. Organomet. Chem., 1973, 50, 17.
- (118) K. Hoffmann and E. Weiss, J. Organomet. Chem., 1973, 50, 25.
- (119) L. Chao and R. Rieke, J. Org. Chem., 1975, 40, 2253.
- (120) L. Chao and R. Rieke, Synth. React. Inorg. Met-Org. Chem., 1975, 5, 165.

- (121) M.J.S. Gynane and I.J. Worrall, J. Organomet. Chem., 1974, 81, 329.
- (122) A. Haaland, Topics in Current Chemistry, 1975, 53, 1.

VITA AUCTORIS

BORN:

May 19, 1947; Concepcion, Chile

ACADEMIC:

1969 - 1974 Universidad de Concepcion, Licenciado en Quimica, 1975

1976 - 1981 University of Windsor, Candidate for the Degree of Doctor of Philosophy (Chemistry)

PUBLICATIONS:

1. "Some Reactions of Copper(I) and Copper(II) with Sulfur Ligands Related to Dimethyldithiocarbamic Acid", a Dissertation submitted to the Chemistry Department, University of Concepcion, in partial fulfillment of the requirements for the degree of Licenciado en Quimica, University of Concepcion, 1974.
2. "Oxidation of Tetramethylthiuram Monosulfide:", J. Inorg. Nucl. Chem., 1975, 37, 1327.
3. "Reactions of Copper(II) Halides and Tetramethylthiuram Sulfide", Bol. Soc. Chil. Quim., 1978, 23, 28.
4. "Reactions of Copper(II) Halides and Tetramethylthiuram Sulfide, II. - Decomposition Reactions and Alternative Routes to the Preparation of Some Intermediates", Bol. Soc. Chil. Quim., 1979, 24, 26.
5. "Coordination Compounds of Indium. 34. - Preparative and Spectroscopic Studies of InX_3Y^- and InX_2Y_2^- Anions. ($\text{X} \neq \text{Y} = \text{Cl}, \text{Br}, \text{I}$)", Inorg. Chem., 1980, 19, 34.
6. "Coordination Compounds of Indium. 37.- ^{115}In -NMR Studies of Anionic Indium Species in Nonaqueous Solutions", Inorg. Chem., 1980, 19, 3432.
7. "Coordination Compounds of Indium. 38.- Complexes of In(I) and In(III) with Macrocyclic Ligands", J. Chem. Soc., Dalton Trans., 1981, 928.
8. "Neutral Adducts of Indium(II)", accepted for publication.
9. "A Facile Synthesis of Cyclopentadienylindium(I)", accepted for publication.